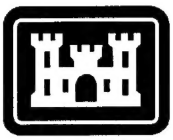

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Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Soil Using GC-ECD

Marianne E. Walsh and Thomas A. Ranney

August 1999

Abstract: Nitroaromatic, nitramine, and nitrate ester explosives are analytes of interest for hazardous waste site characterization and land mine detection. Traditionally determined by high-performance liquid chromatography (HPLC), these thermally labile analytes may be determined by gas chromatography (GC) by using direct injection into a deactivated liner and a short (6-m) wide-bore capillary column. Gas chromatography-electron capture detector (GC-ECD) and HPLC-ultraviolet (UV) concentration estimates of these compounds in field-contaminated soils from hazardous waste sites were compared, and excellent correlation ($r > 0.97$) was found between the two methods of analysis for the compounds most frequently detected: 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene (TNB), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). GC-ECD method detection limits (MDL) were about 1 µg/kg for the di- and trinitroaromatics, about 10 µg/kg for the mononitroaromatics, 3 µg/kg for RDX, 25 µg/kg for HMX, and between 10 and 40 µg/kg for the nitrate esters (NG and PETN).

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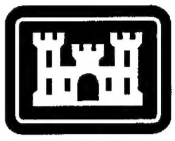

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PREFACE

This report was prepared by Marianne E. Walsh, Chemical Engineer, Geological Sciences Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire, and Thomas A. Ranney, Staff Scientist, Science and Technology Corporation, Hanover, New Hampshire.

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Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Soils Using GC-ECD

MARIANNE E. WALSH AND THOMAS A. RANNEY

INTRODUCTION

The electron capture detector (ECD) has been used for many years to detect trace levels of explosives. The selectivity and sensitivity of the ECD to the nitro group common to most explosives have made the ECD the most commonly used gas chromatographic detector for explosives residues in environmental samples, especially in forensic applications (Yinon and Zitrin 1993). Gas chromatographic analysis of solvent extracts of environmental matrices can be problematic, especially for the thermally labile nitramine and nitrate ester explosives. Thus gas chromatography (GC) has not been used routinely for quantitative analyses of explosives residues in soil. Recently we developed an analytical method for explosives in drinking water that was based on solid-phase extraction (SPE) and determination by GC-ECD (Walsh and Ranney 1998). This paper describes the analysis of soil extracts using gas chromatographic conditions similar to those used to analyze water extracts.

Traditionally, determination of explosives in soil served either forensic or hazardous waste investigations. More recently, there is interest in ultrasensitive methods for determining explosives in soil that could be used to detect buried land mines (Rouhi 1997).

Jenkins et al. (1989) developed what is now the standard method for explosives in soil (SW-846 Method 8330 [USEPA 1994]) to characterize military sites contaminated with explosives residues from the production or use of high explosives munitions. For this standard analytical method, a 2-g soil sample is extracted by 18 hours of sonication with 10 mL of acetonitrile (AcN). The AcN extract is mixed 1:1 (v/v) with aqueous calcium chloride to flocculate fines prior to filtration and analysis by high-performance liquid chromatography with an ultraviolet detector (HPLC-UV). Explosives concentrations of 1 mg/kg (1 ppm) or higher may be determined using this procedure, and detection limits are sufficiently low for human health or ecological risk assessments. Jenkins et al. chose HPLC-UV rather than GC for several reasons: compatibility of the thermally labile analytes with room temperature chromatographic separation, large linear range of the detector, ruggedness of the method, ability to analyze high concentration (>40 µg/L) water samples by direct injection, and compatibility of the solvent (acetonitrile) used to extract soils with reversed-phase HPLC.

In the 1970s, Jenkins, Leggett, and Murrmann used GC-ECD when they characterized the vapors from military-grade TNT in conjunction with efforts to detect buried land mines by sampling the atmosphere (Murrmann et al. 1971, Jenkins et al. 1974, and Leggett et al. 1977). Some solvent (benzene) extracts of soil were analyzed as well. Instrumentation at that time was not conducive to quantitative determination of explosives in soil, especially on a routine basis.

Improvements in injection port liners, GC columns, and most recently the ECD detector (David et al. 1997) have led us to reexamine the utility of the GC-ECD for determination of explosives in soil for both hazardous waste site characterization and mine detection.

Analytes of interest differ somewhat for hazardous waste characterization and mine detection (Table 1). Soil that was contaminated by the manufacture or use of explosives most likely contains

Table 1. Analytes of interest for two applications of analytical methods for explosives in soil: Hazardous waste characterization and mine detection.

Analyte	*Class*	*Abbreviation*	*CAS* number*	*Haz. waste char.*	*Mine detection*
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	nitramine	HMX	2691-41-0	√	
Hexahydro-1,3,5-trinitro-1,3,5-triazine	nitramine	RDX	121-82-4	√	√
1,3,5-Trinitrobenzene	nitroaromatic	TNB	99-35-4	√	
1,4-Dinitrobenzene	nitroaromatic	1,4-DNB	100-25-4		√
1,3-Dinitrobenzene	nitroaromatic	1,3-DNB	99-65-0	√	√
1,2-Dinitrobenzene	nitroaromatic	1,2-DNB	528-29-0		√
2,4,6-Trinitrophenylmethylnitramine	nitroaromatic/ nitramine	Tetryl	479-45-8	√	
Nitrobenzene	nitroaromatic	NB	98-95-3	√	
2,4,6-Trinitrotoluene	nitroaromatic	2,4,6-TNT	118-96-7	√	√
4-Amino-2,6-dinitrotoluene	amino-nitroaromatic	4-Am-DNT	1946-51-0	√	√
2-Amino-4,6-dinitrotoluene	amino-nitroaromatic	2-Am-DNT	355-72-78-2	√	√
2,4-Dinitrotoluene	nitroaromatic	2,4-DNT	121-14-2	√	√
2,6-Dinitrotoluene	nitroaromatic	2,6-DNT	606-20-2	√	√
2-Nitrotoluene	nitroaromatic	2-NT	88-72-2	√	
3-Nitrotoluene	nitroaromatic	3-NT	99-08-1	√	
4-Nitrotoluene	nitroaromatic	4-NT	99-99-0	√	
3,5-Dinitroaniline	amino-nitroaromatic	3,5-DNA	618-87-1	√	
Nitroglycerine	nitrate ester	NG	55-63-0	√	
Pentaerythritoltetranitrate	nitrate ester	PETN	78-11-5	√	

*Chemical Abstract Service Registry Number

TNT and RDX (Walsh et al. 1993), the explosives most commonly found in military-grade explosives (Department of the Army 1984). Co-contaminants such as manufacturing by-products and biodegradation products may also be present. More recently, we have found that HMX may be present in high concentrations in soils from anti-tank firing ranges where octol-filled (70% HMX:30% TNT) rockets have been fired (Jenkins et al. 1997, 1998).

For land mine detection, the analytes of interest are the constituents of TNT vapor, principally the isomers of DNT, DNB, and TNT (Jenkins et al. in prep). Although not known at this time, RDX, which has minimal vapor pressure, may be of interest due to its mobility in soil following aqueous dissolution.

EXPERIMENTAL METHODS

Matrices

Field-contaminated soils were from Iowa Army Ammunition Plant (AAP), Milan AAP (Tennessee), Nebraska Ordnance Plant, Monite (Nevada), Eagle River Flats Open Burning/Open Detonation (OB/OD) Pad (Alaska), Raritan Arsenal (New Jersey), Savanna Army Depot (Illinois), Chickasaw Ordnance Works (Tennessee), U.S. Naval Ammunition Depot (Georgia), Camp Shelby (Mississippi), Fort Ord (California), CFB-Valcartier (Quebec), Sandia (New Mexico), and Fort Leonard Wood (Missouri).

Blank matrices were Ottawa sand, an Army Environmental Center (AEC) standard soil obtained from Rocky Mountain Arsenal (Colorado), a soil from Fort Leonard Wood, and a silt obtained locally in Hanover, New Hampshire.

Calibration

Standards were prepared from standard analytical reference material (SARM) from the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland, or obtained commercially from Supelco and Restek. All solutions were prepared in acetonitrile. Calibration standards were prepared fresh each day over the range 0.4 to 100 µg/L from 10 mg/L combined stock solutions that were stored at –22°C in the dark.

Extraction

Archived field-contaminated soils were chosen based on previous HPLC analysis that indicated the presence of several of the Method 8330 analytes over a wide concentration range (Table A1). Following the soil extraction procedure specified by Method 8330, 2-g soil subsamples were extracted with 10 mL of acetonitrile (with no internal standard) for 18 hours in a cooled sonic bath. To compare concentration estimates obtained by GC to those obtained by HPLC, the extracts were split. For GC analysis, a portion of each acetonitrile extract was filtered through a Millex SR filter unit (Millipore). For HPLC analysis, an aliquot of each acetonitrile extract was mixed with an equal volume of aqueous calcium chloride prior to filtration through a Millex SR filter unit.

Additional archived soils that had trace analytes, based on previous HPLC analysis, were extracted using a higher soil-to-solvent ratio (25 g soil:50 mL acetonitrile). For each soil, duplicate 25-g subsamples were extracted with 50 mL of acetonitrile in a cooled sonic bath for 18 hours. If enough soil was available, matrix spikes (MS) and matrix spike duplicates (MSD) were also prepared and extracted. Soils were spiked with 5 mL of a spike solution (50 µg/L nitroaromatics and 200 µg/L RDX) and left to air-dry for 24 hours in a fume hood. The spike solution contained the analytes of interest for mine detection (Table 1). The spiked concentration in soil was 10 µg/kg for nitroaromatics and 40 µg/kg for RDX. All samples were extracted with 50 mL of acetonitrile containing 3,4-DNT (25 µg/L) as an internal standard. These samples were also extracted for 18 hours in a cooled sonic bath. Prior to GC analysis, extracts were filtered through Millex SR filter units. Prior to HPLC analysis, 0.5 mL of each filtered acetonitrile extract was mixed with 2 mL of reagent-grade water (MilliQ).

Soils collected from an experimental minefield at Sandia were extracted without air-drying using 2 g soil:10 mL acetonitrile and 25 g soil:50 mL acetonitrile. Soils from Fort Leonard Wood were extracted without air-drying using 2 g soil:5 mL acetonitrile or 20 g soil:50 mL acetonitrile.

Preconcentration

Solid-phase extraction

A limited number of acetonitrile extracts were preconcentrated using solid-phase extraction. From some of the soils extracted with 50 mL of acetonitrile, the solvent remaining above the soil was slowly decanted. The volume of the decanted solvent was measured (30–40 mL), then the solvent was mixed with 500 mL of reagent-grade water. Previous work has shown that the analytes of interest will be retained by the solid phase if the aqueous concentration of acetonitrile is less than 10%.* For each sample, an Empore styrene-divinyl benzene reverse phase sulfonated resin (SDB-RPS) disk was placed on a vacuum filter apparatus and preconditioned according to manufacturer's directions: rinsing with 10 mL each of acetone, isopropanol, and methanol. For the final organic solvent rinse, a 20-mL aliquot of acetonitrile was used. The acetonitrile was pulled through each disk, followed by reagent-grade water, and then the 500-mL AcN/water sample. The disk was rinsed with a 20-mL aliquot of distilled water to remove salts. Air was then pulled through each membrane for 20 minutes to remove excess water. Finally, the disks were eluted using 5 mL of acetonitrile.

Salting-in preconcentration

A limited number of soil extracts were preconcentrated by mixing 40 mL of acetonitrile soil extract with aqueous sodium chloride (65 g NaCl:200 mL reagent-grade water) (Jenkins and Miyares 1991). After vigorous mixing and phase separation, approximately 3.5 mL of acetonitrile extract was recovered, yielding a concentration factor of 11.

Method detection limits and spike recovery

Method detection limits (MDL) and spike recoveries were determined using the two soil:solvent ratios used for the extraction of field samples. Following the Method 8330 protocol, seven replicate 2-g soil samples (either Ottawa sand or AEC standard soil) were spiked with 1 mL of 10- or 100-µg/L spike solutions to yield 5- and 50-µg/kg samples containing the analytes of interest for hazardous waste site characterization (Table 1). After one hour, 9 mL of acetonitrile was added and the samples extracted for 18 hours in a cooled sonic bath. At two hours into the sonication period, a small aliquot of the extract was taken for analysis to determine the stability of NG and PETN in a cooled sonic bath.

A second set of Ottawa sand samples was

*Personal communication, Philip G. Thorne, Geological Sciences Division, CRREL, Hanover, New Hampshire, 1998.

spiked by adding either 1 mL or 5 mL of a 50-µg/L solution to 25-g soil samples to yield 2-µg/kg and 10-µg/kg samples for the nitroaromatics of interest for mine detection (Table 1). The spike solution also contained RDX at a concentration four times greater than the nitroaromatics. The samples spiked with 1 mL were aged uncapped for one hour prior to extraction. The samples spiked with 5 mL were aged 24 hours uncapped. All samples were extracted with 50 mL of acetonitrile containing 3,4-DNT (25 µg/L) as an internal standard. These samples were also extracted for 18 hours in a cooled sonic bath.

Similar spike recovery studies were performed with other matrices, including glass beads (25-micron, 3M Company), silt (dry and wet), and AEC soil.

Instrumentation

GC-ECD

Initially we used an HP 5890 equipped with an Ni^{63} ECD. Later, we used an HP 6890 equipped with a micro cell Ni^{63} ECD. For both GCs, we used direct injection (250°C) of 1-µL samples. The injection port liner was a deactivated Restek Uniliner. The analytical columns were 6-m- by 0.53-mm-ID fused-silica, 1.5-µm film thickness of either 100% polydimethylsiloxane (J and W DB-1) or (5%-phenyl)-methylsiloxane (HP-5). The GC oven was temperature-programmed as follows: 100°C for 2 min, 10°C/min ramp to 200°C, 20°C/min ramp to 250°C, 5 min hold. The carrier gas was hydrogen or helium at 12 to 15 mL/min. The makeup was nitrogen (30 to 40 mL/min). Confirmation columns were Restek RTX-200 (Crossbond trifluoropropyl methylpolysiloxane) and Restek RTX-225 (50% cyanopropylmethyl–50% phenyl methylpolysiloxane). Details of the procedure may be found in SW-846 Method 8095 (USEPA 1998).

HPLC-UV

Initial studies used the HPLC separation specified in Method 8330. A 25-cm by 4.6-mm (5-µm) octadecyl (Supelco LC-18) column was eluted with 1.5 mL/min 1:1 methanol:water. Two alternative separations to achieve resolution of DNB, DNT, and Am-DNT isomers used either a 25-cm by 4.6-mm (5-µm) octadecyl (Burdick and Jackson OD5) column eluted with 1.4 mL/min 33:13:54 methanol:acetonitrile:water or a 15-cm by 3.9-mm (4-µm) Nova Pak C_8 (Waters Millipore) column eluted with 1.4 mL/min 15:85 isopropanol:water. The confirmation separation was on a 25-cm by 4.6-mm (5-µm) cyano (Supelco LC-CN) column eluted with either 1.5 mL/min 1:1 methanol:water or 1.2 mL/min 12:13:62 methanol:acetonitrile:water. Injection volume for each separation was 100 µL. Following these HPLC separations, absorbance was recorded at 254 nm on a Spectra Physics Spectra 100 variable wavelength UV detector.

RESULTS

Field-contaminated soils: Concentration estimates by GC-ECD and HPLC-UV

Wide concentration range

To test the feasibility of using GC-ECD for the analysis of soil extracts, we chose 24 archived field-contaminated soils that contained several of the analytes of interest over a wide range of concentration (based on previous HPLC analysis) and a variety of sites across North America. Because some of these soils were analyzed by HPLC over a decade ago, we repeated an HPLC analysis along with the GC analysis using extract splits from 2-g soil aliquots extracted with 10 mL of acetonitrile. We used the standard HPLC separation initially, then for those soils containing isomers of DNT and Am-DNT, extracts were reanalyzed using one of the alternative HPLC separations described above.

For GC, extracts were analyzed on the HP 5890 where the ECD had a very limited linear range. All extracts were diluted by at least a factor of 10 and some up to 10^6 to be within the calibration range. These large dilutions probably prevented the deposition of high boiling point residues in the injection port liner and on the head of the GC column, a potential problem that concerns us when GC is used routinely for the analysis of soil extracts.

Results of these analyses are shown in Table A1. We correlated the GC concentration estimates with those obtained by HPLC for those analytes that were detected 10 or more times out of the 24 samples. The most frequently detected analytes were TNT (18 times), RDX (11 times), 2,4-DNT (15 times), TNB (19 times), DNB (12 times), and HMX (10 times). All correlation coefficients (Fig. 1) were greater than 0.97. However, with the exception of DNB, slopes of the least squares regression models were significantly different from the expected value of 1.00. For TNT, RDX, and 2,4-DNT, slopes were all greater than 1.00. Because concentrations for each of these analytes spanned over six orders of magnitude, this difference in slope may be an

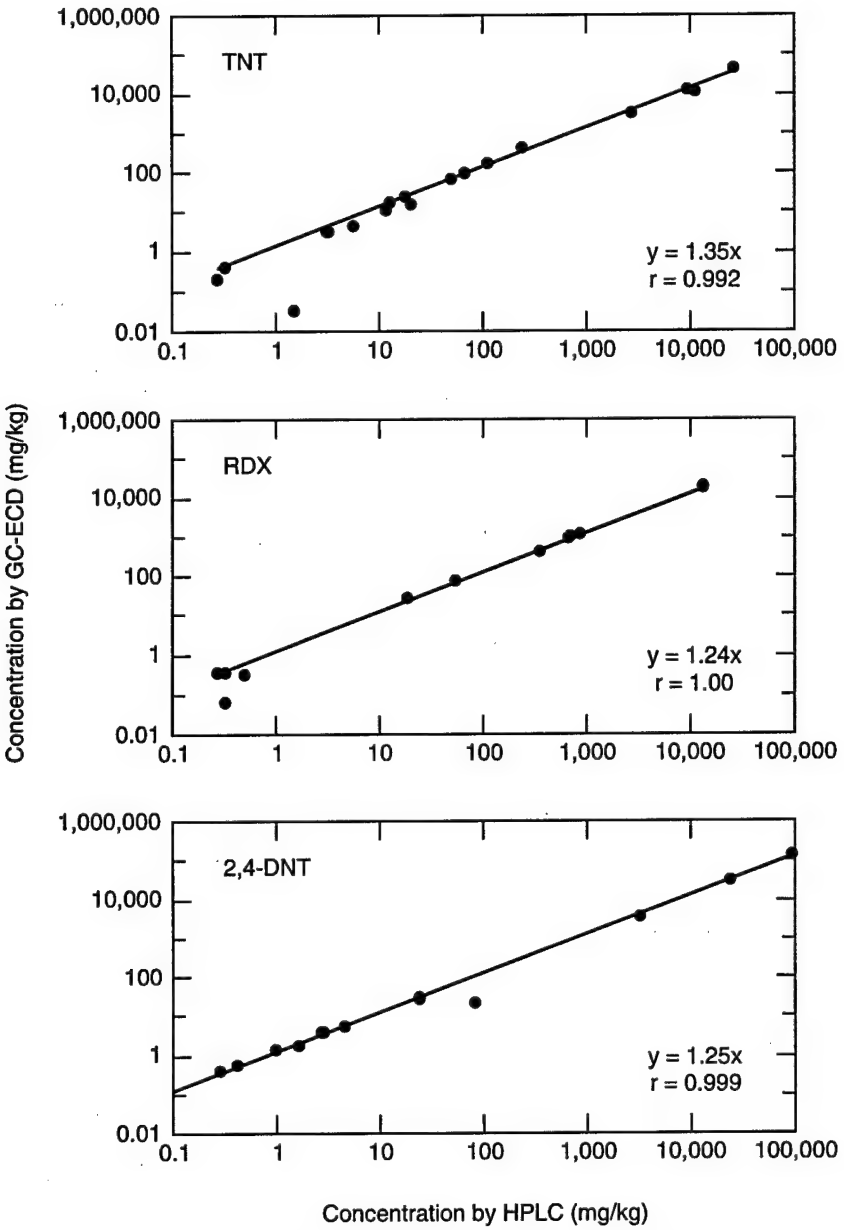


Figure 1. Correlation analysis of GC-ECD concentration (mg/kg) estimates with those from HPLC-UV analysis using splits of the same acetonitrile extract (2 g soil:10 mL acetonitrile) from archived soils.

artifact of the experimental error associated with the large dilutions required for GC and the dominance of high values on the slope obtained from a least-squares model. Two other problems were the considerable scatter in the TNB data and the underestimation of HMX by GC. The TNB scatter is most likely due to TNB's instability in solution, and the underestimation of HMX is likely due to thermal degradation during the GC analysis. Although accurate GC analysis of HMX is possible, the first peak to degrade in shape following multiple injections of water or soil extracts is the HMX peak. Despite these problems, we decided that GC analysis of soil extracts was feasible. The GC offered two significant advantages over the standard HPLC method: lower detection levels and improved chromatographic resolution of the isomers of DNT and Am-DNT.

One important advantage of using both HPLC and GC analysis is the ability to independently

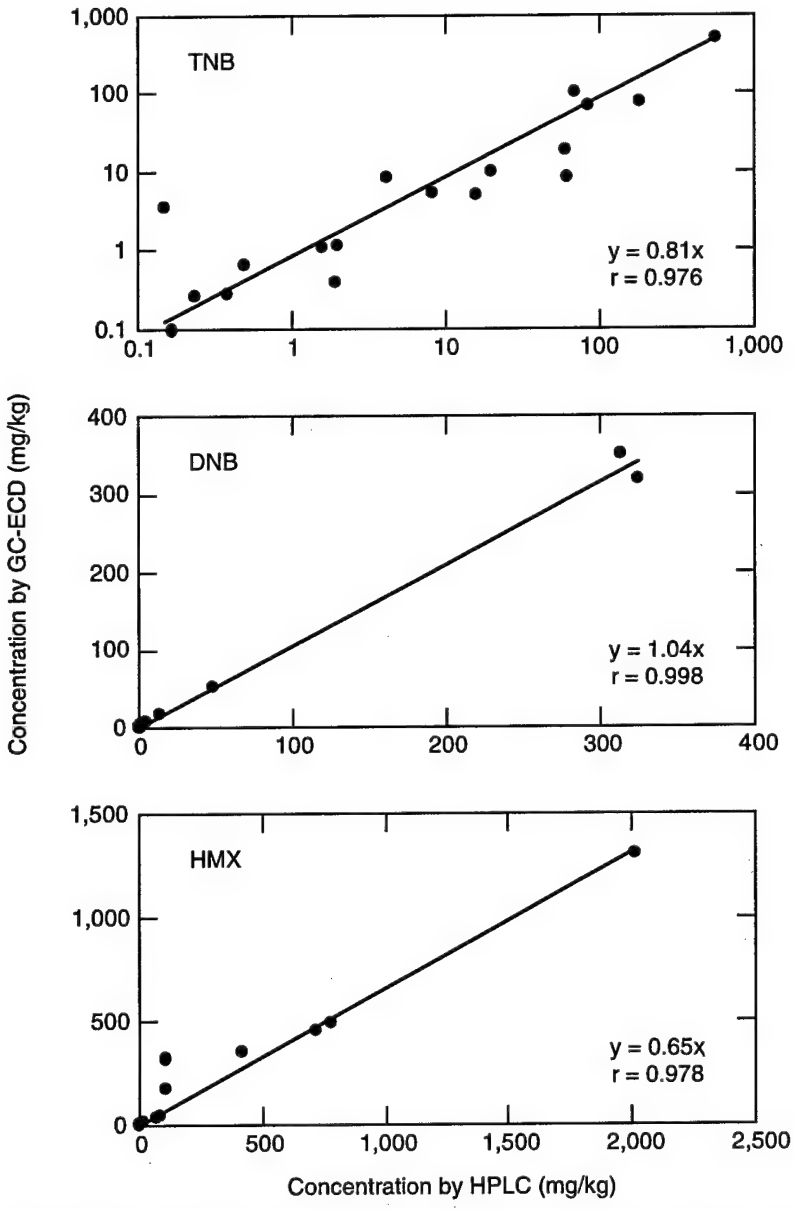


Figure 1 (cont'd). Correlation analysis of GC-ECD concentration (mg/kg) estimates with those from HPLC-UV analysis using splits of the same acetonitrile extract (2 g soil:10 mL acetonitrile) from archived soils.

confirm analyte identities in complex chromatograms. This advantage was apparent for one of the Monite soils. Chromatograms from previous HPLC analyses were thought to show a peak for TNT, but TNT was not detected by GC. Rather, the GC showed peaks for several isomers of DNT, one of which (3,4-DNT) co-elutes with TNT using the standard HPLC analytical separation and another (3,5-DNT) that coelutes with TNT using the standard confirmation HPLC separation.

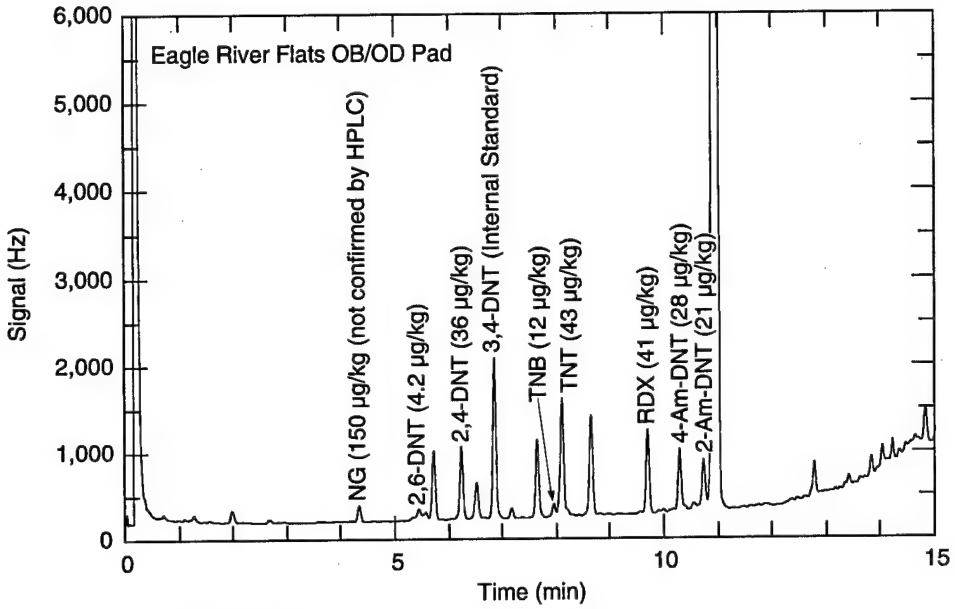
Trace concentrations

Another series of archived soils was selected for extraction and analysis. For land mine detection, very low (1 µg/kg) concentrations may need to be detected, and we selected soils for which previous HPLC analysis had either shown trace (less than the detection limit) concentrations of either TNT, 2,4-DNT, or RDX, or the soils were collected near samples that had trace concentrations. For the extraction of these soils we used 25-

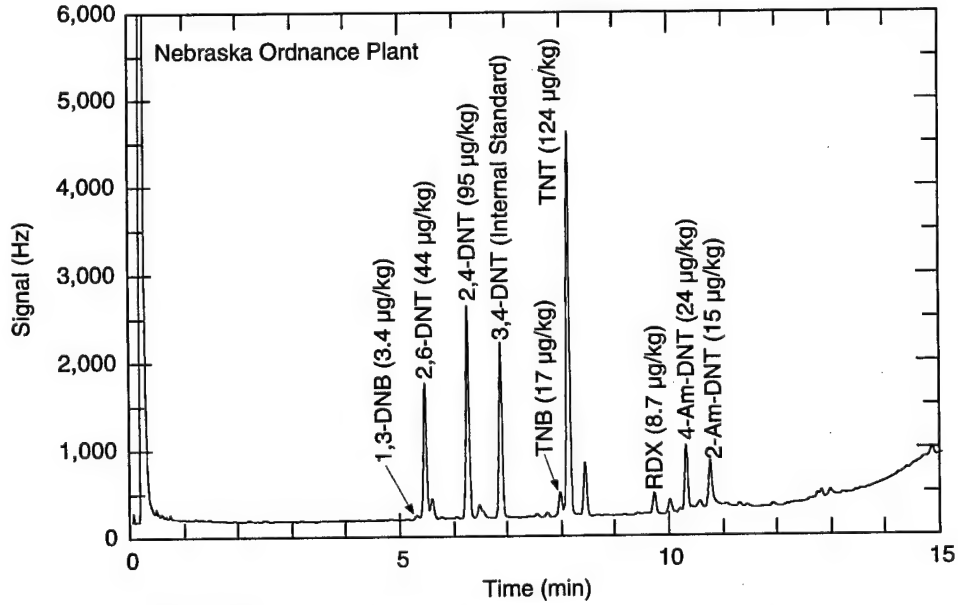
g soil subsamples and 50 mL of acetonitrile containing 25-µg/L 3,4-DNT as an internal standard. If enough soil was available, MS/MSD were also prepared.

The GC analysis was conducted on an HP 6890 equipped with a µ-ECD. No dilutions were performed for the GC analysis. For the HPLC analysis, we used the Nova Pak C_8 (Waters Millipore) separation described above. Example chromatograms of real soil extracts are shown in Figure 2.

TNT was detected by GC in all 13 extracts ranging from 1.3 to 273 µg/kg (Table A2). For duplicates, the median relative percent difference (RPD%) was 11%. One sample (Camp Shelby) showed very poor agreement between replicates. This sample had 2,4-DNT as the highest concen-

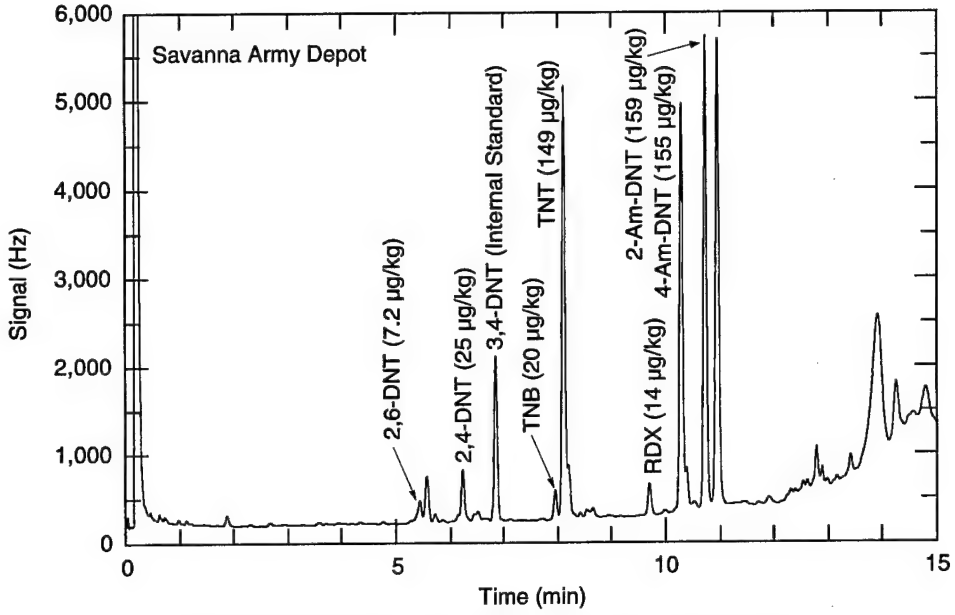


a) GC-ECD analytical column (HP-5), Eagle River Flats.

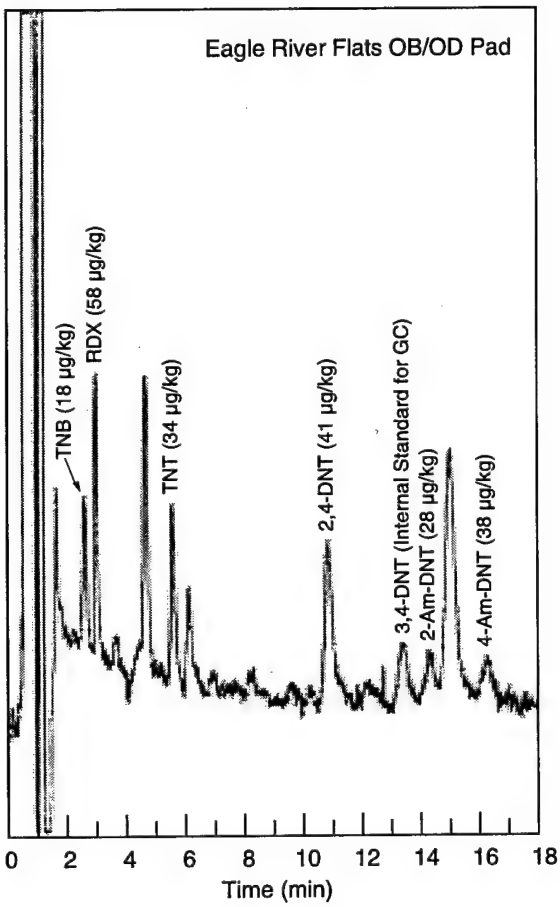


b) GC-ECD analytical column (HP-5), Nebraska Ordnance Plant.

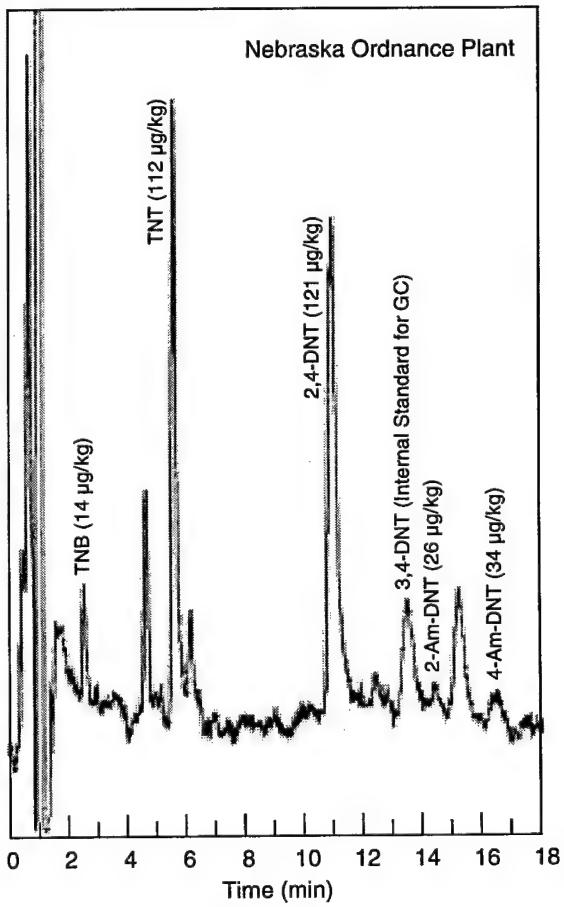
Figure 2. Chromatograms from field-contaminated soils (25 g extracted with 50 mL acetonitrile).



c) GC-ECD analytical column (HP-5), Savanna Army Depot.

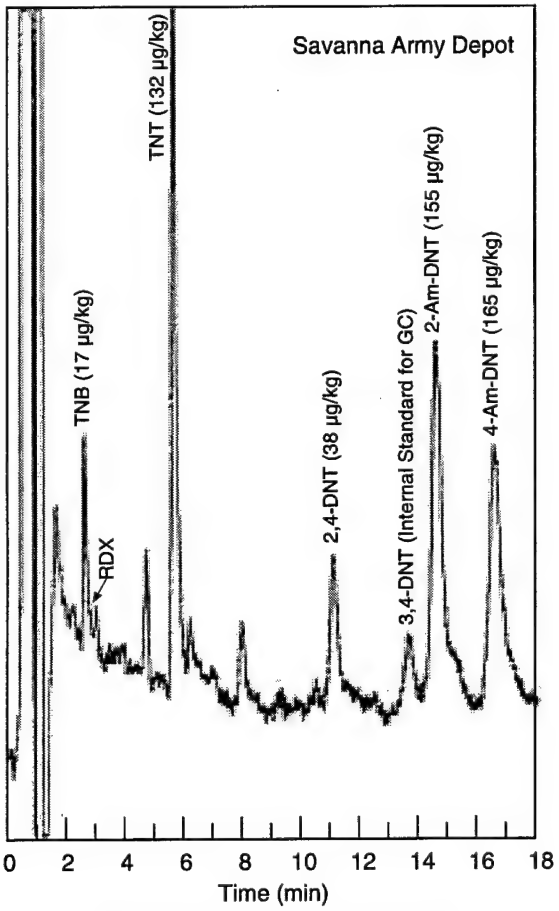


d) HPLC-UV, Eagle River Flats.

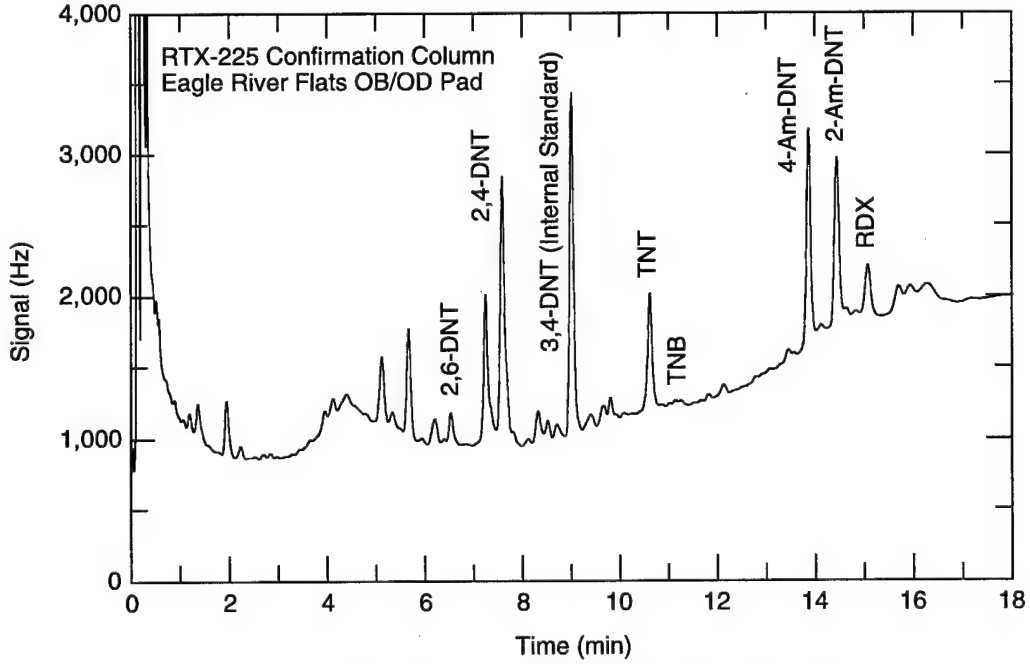


e) HPLC-UV, Nebraska Ordnance Plant.

Figure 2 (cont'd). Chromatograms from field-contaminated soils (25 g extracted with 50 mL acetonitrile).

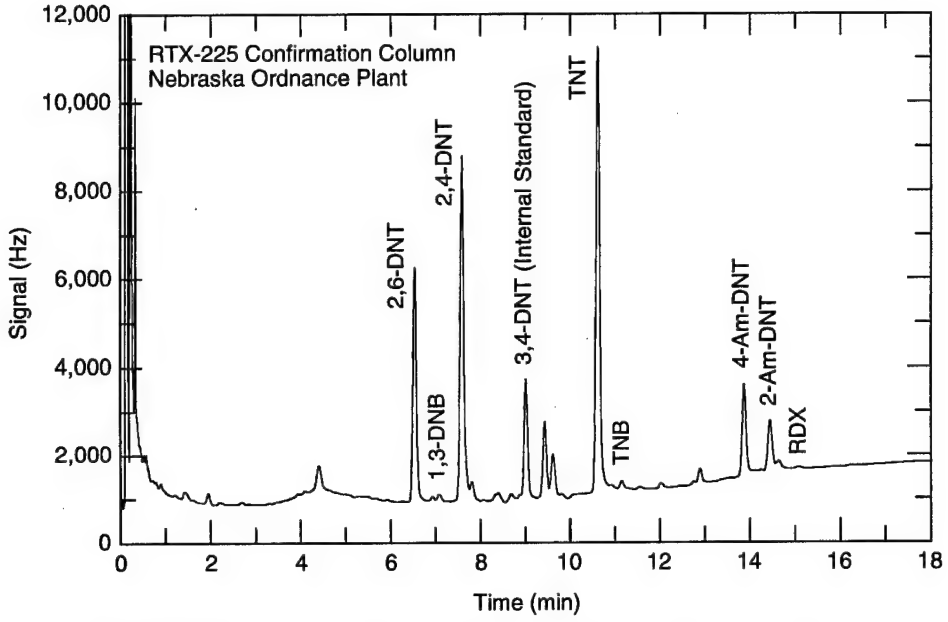


f) HPLC-UV, Savanna Army Depot.

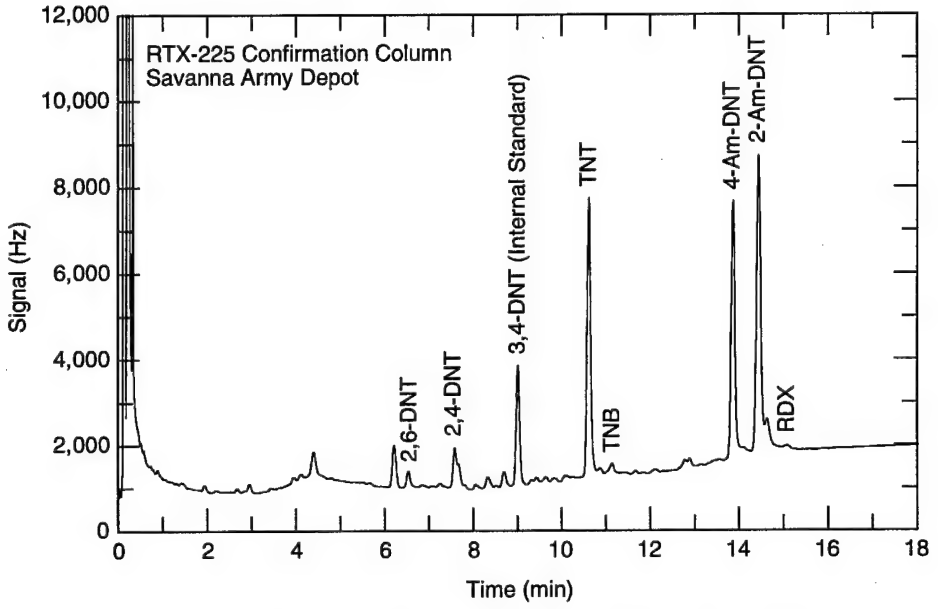


g) GC-ECD confirmation column (RTX-225), Eagle River Flats.

Figure 2 (cont'd).

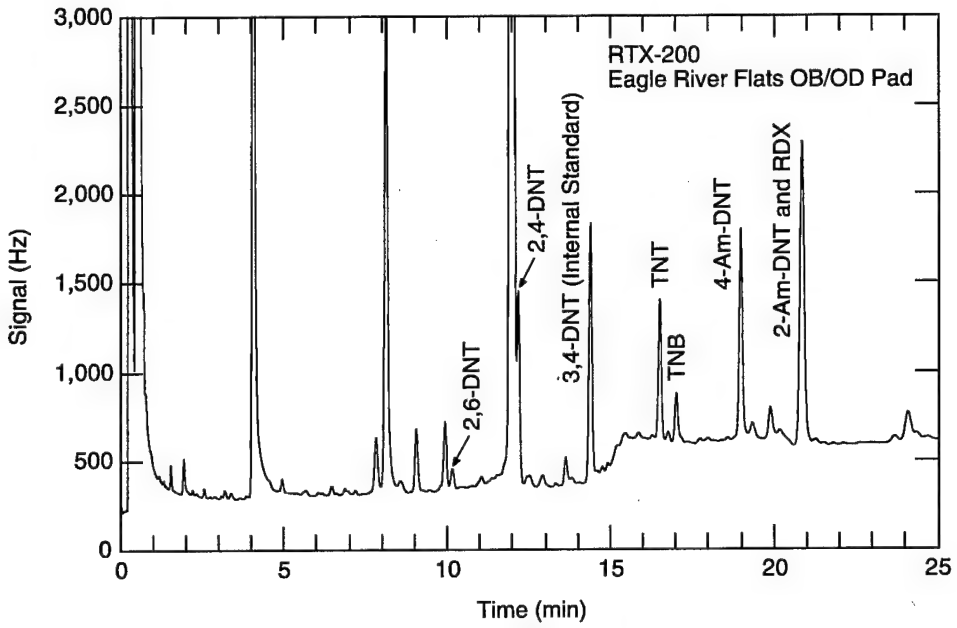


h) GC-ECD confirmation column (RTX-225), Nebraska Ordnance Plant.

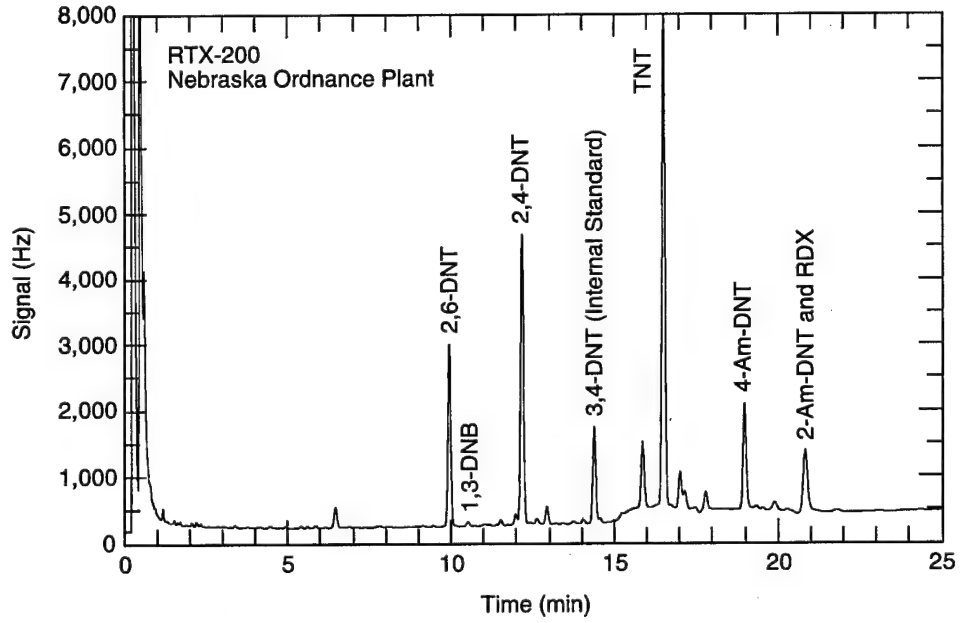


i) GC-ECD confirmation column (RTX-225), Savanna Army Depot.

Figure 2 (cont'd). Chromatograms from field-contaminated soils (25 g extracted with 50 mL acetonitrile).

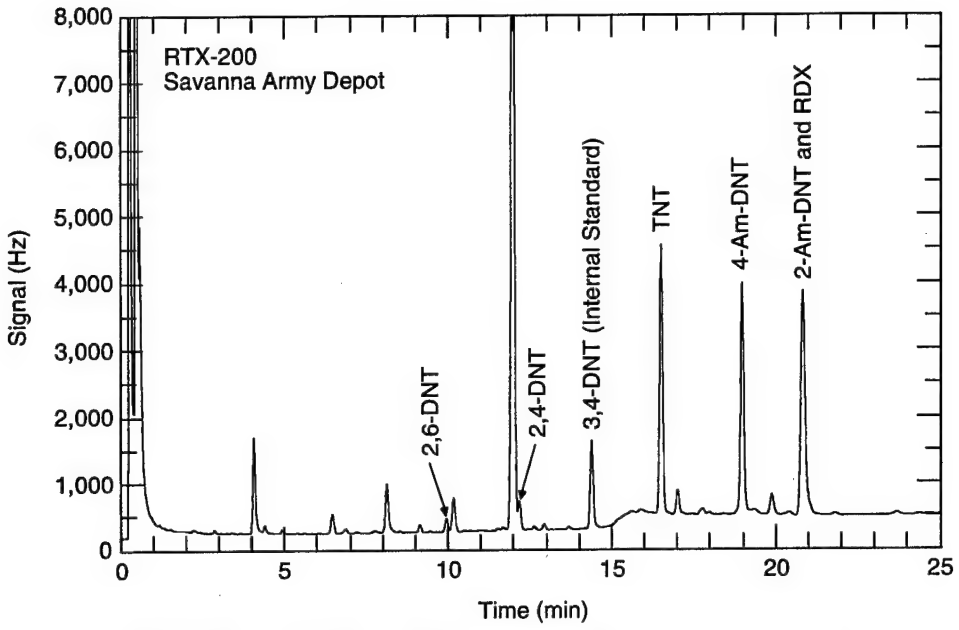


j) GC-ECD confirmation column (RTX-200), Eagle River Flats.



k) GC-ECD confirmation column (RTX-200), Nebraska Ordnance Plant.

Figure 2 (cont'd).



l) GC-ECD confirmation column (RTX-200), Savanna Army Depot.

Figure 2 (cont'd). Chromatograms from field-contaminated soils (25 g extracted with 50 mL acetonitrile).

tration analyte, and the TNT, in this case, was probably present as in impurity in 2,4-DNT, not as a high-explosive residue. We found 2,4-DNT in 11 of the 13 extracts, over the concentration range 0.94 to 8587 µg/kg (Table A2). Two of the soils showed extreme heterogeneity for this analyte with concentration estimates of 36 and 8587 µg/kg in duplicates for one sample, and 145 and 4096 µg/kg in duplicates for another sample. At the sites where these soils (Eagle River Flats OB/OD Pad and Camp Shelby NE Quad) were collected, propellant grains were scattered across the soil surfaces. 2,4-DNT is a propellant ingredient, and such extreme heterogeneity is consistent with particulate contamination, such as from a propellant grain fragment. In the samples with relatively high 2,4-DNT concentrations, 2,6-DNT and 3,4-DNT were also detected by GC. These two isomers co-eluted on the HPLC separation. Thus, 3,4-DNT is not suitable as an internal standard for extracts from soils contaminated with high concentrations of 2,4-DNT.

The Am-DNT isomers were detected in 10 of the 13 soils by GC (Table A2). For the samples from Fort Ord, several unidentified peaks eluted near the Am-DNTs on the GC analysis and made quantification difficult. Similar interferences were not observed in other soils, although an unidentified peak did elute after 2-Am-DNT from four other soils (Fig. 2). We preconcentrated a few samples using solid-phase extraction to see if the analytes of interest would preferentially be retained on the solid-phase disk. This very time-consuming sample preparation step did not provide any benefits in terms of cleanup or detectability. Rather, all peak heights, analytes and interferences, increased in proportion to the preconcentration.

The only DNB isomer detected was 1,3-DNB, which we found in two of the soils at around 5 µg/kg (Table A2).

Recoveries from the MS/MSD samples were excellent in some samples and low in others (Table A2). Matrix effects are discussed later.

TNT and 2,4-DNT concentrations above 20 µg/kg were quantifiable by HPLC, and we correlated the GC concentrations estimates (including the MS/MSD without subtracting the spiked amount) with those newly obtained by HPLC using splits of the same extract. Each data point (Fig. 3) represents a single sample (not a mean of duplicates). Again we found good correlation ($r = 0.997$ for both analytes) between the two methods of determination, and again we found that the slopes of the least-squares models were greater than 1.00 (1.14 and 1.12 for TNT and 2,4-DNT, respectively), indicating slightly higher estimates by GC (Fig. 3).

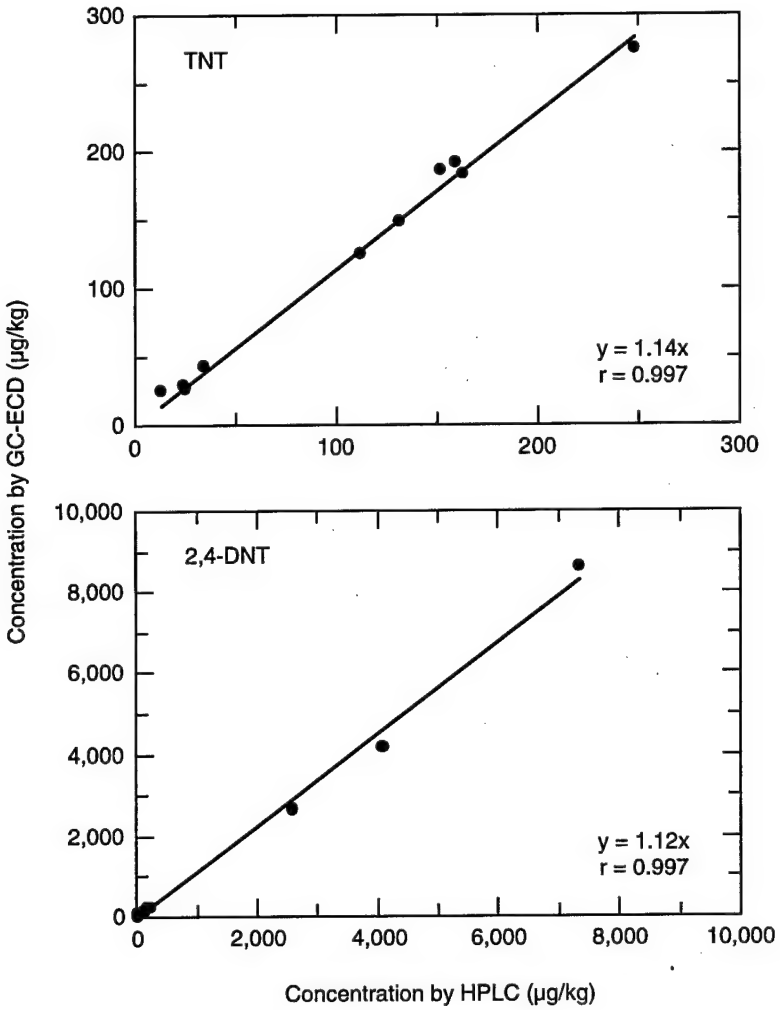


Figure 3. Correlation analysis of GC-ECD concentration (µg/kg) estimates with those from HPLC-UV analysis using splits of the same acetonitrile extract (25 g soil:50 mL acetonitrile) from archived soils.

We observed no degradation in the GC peak shapes or heights despite an extended run with over 70 injections of soil extracts and standards.

Confirmation columns

Because analyte identity is based solely on retention time when using an ECD, confirmation is important. If concentrations are very high, a mass spectrometry or photodiode array detector can yield irrefutable confirmation. For lower concentrations, analysis by GC-ECD with confirmation by HPLC-UV provides confirmation based on different physical properties of the analytes (vapor pressure and polarity for separation, and electronegativity and UV absorption for detection). However, when concentrations are very low (less than 50 µg/kg), we must rely on secondary column confirmation by GC-ECD. Two confirmation columns that are more polar than the HP-5 analytical column were used. They were a Restek RTX-200 (Crossbond trifluoropropyl methylpolysiloxane) and Restek RTX-225 (50% cyanopropylmethyl–50% phenyl methylpolysiloxane). Example chromatograms are shown in Figure 2 and retention times are given in Table A3.

Of these two columns, the RTX-225 was preferred because RDX was resolved from 2-Am-DNT. These analytes co-eluted on the RTX-200. Another problem with the RTX-200 was an intermittent interfering peak eluting just prior to 2,4-DNT. (This peak seemed to be associated with plastics, such as the syringes used during filtration, but was not consistently present.) Neither column was suitable for confirming low concen-

trations of HMX, although a thinner film may have allowed this analyte to elute intact.

Spike recoveries and MDL

We spiked two blank matrices to determine detection limits for the analytes of interest for hazardous waste characterization. We spiked samples at 5 and 50 µg/kg because the ECD response factors differ substantially for these analytes (Fig. 4), being significantly higher for the di-and trinitroaromatics. Each matrix had interferences (Fig. 5) that inflated the MDL for some of the

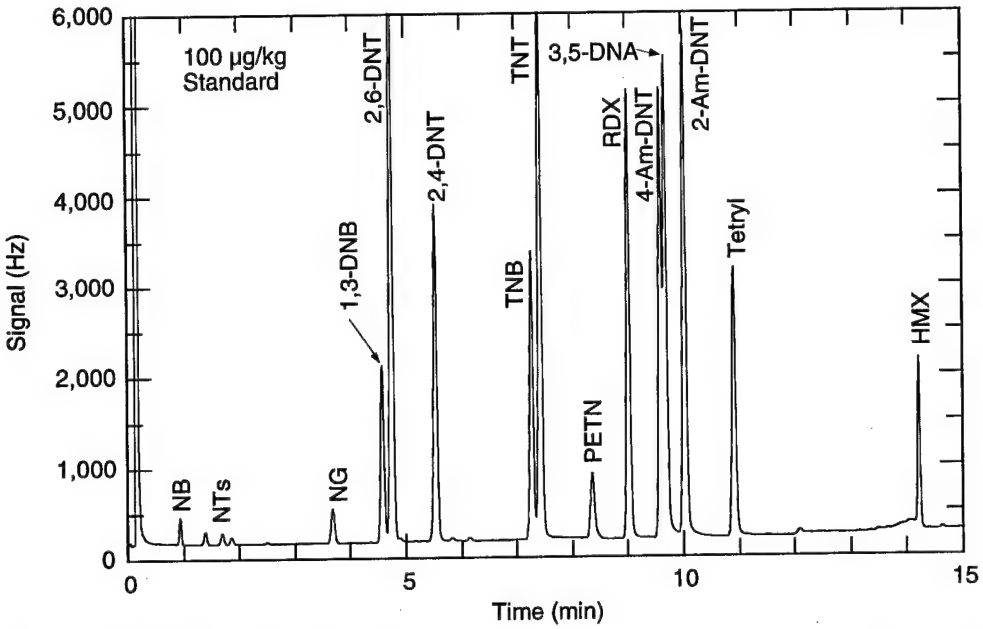
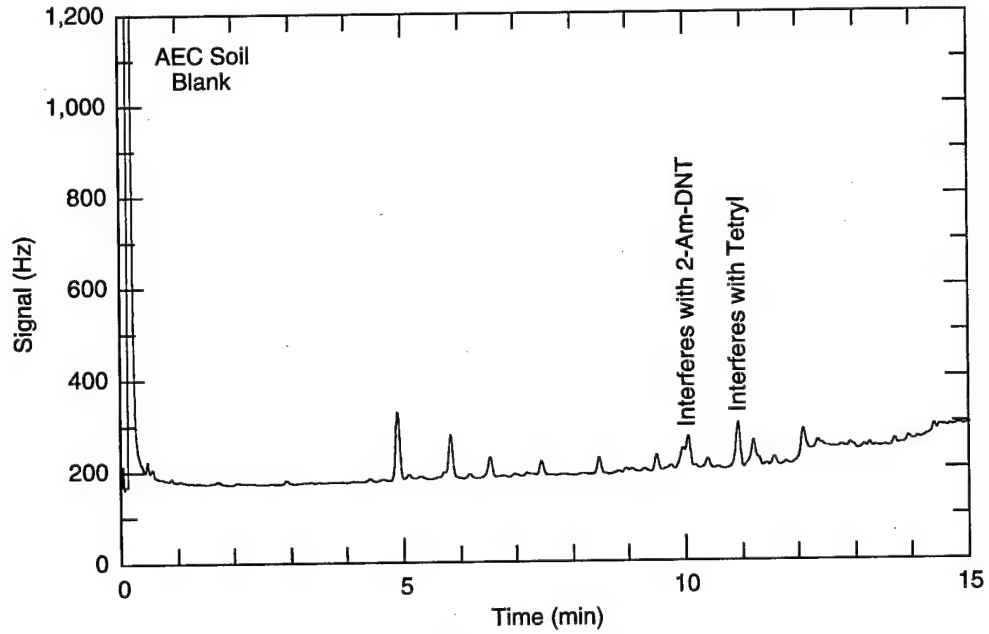


Figure 4. GC-ECD chromatogram of calibration standard containing the analytes of interest for hazardous waste site characterization.

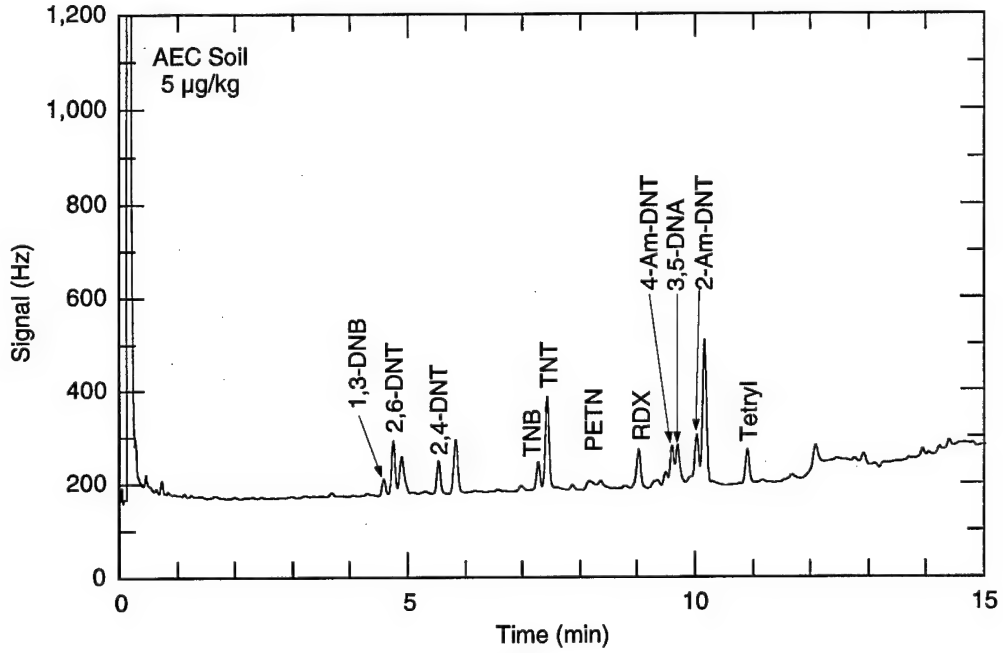


a) AEC soil, blank.

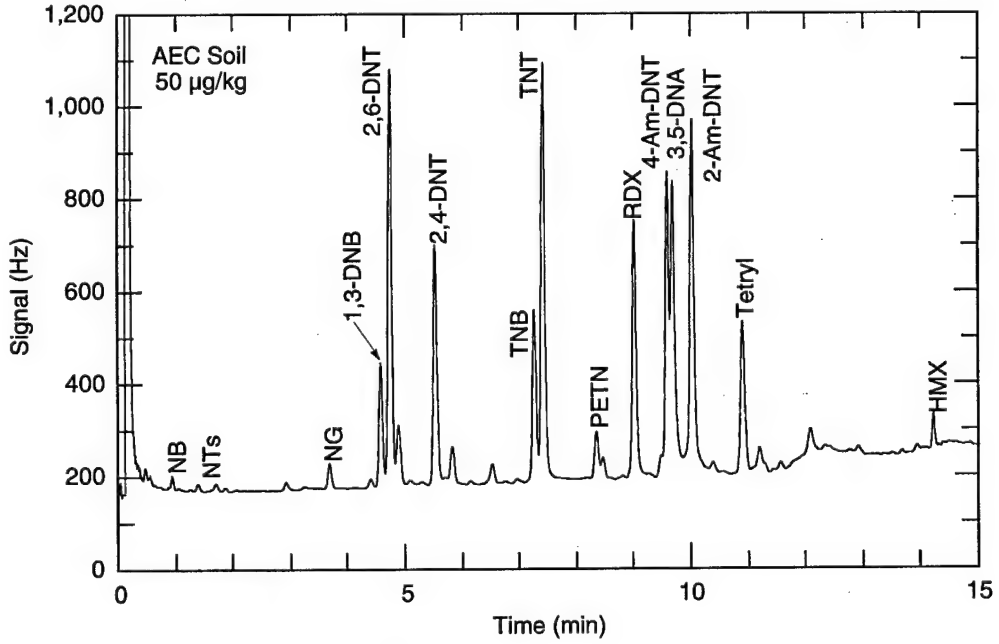
Figure 5. GC-ECD chromatograms of blank and spiked soils used for determination of method detection limits and spike recovery.

analytes (TNT in the Ottawa sand and 2-Am-DNT and tetryl in the AEC soil). Nonetheless, the MDL (Table 2, Table A4) were generally about 1 µg/kg for the di- and trinitroaromatics and 10 times higher for the mononitroaromatics, which is consistent with the variable response factors of the ECD for these compounds (Fig. 4, 5). MDL were between 1 and 3 µg/kg for the aminonitrotoluenes, and were quite variable for the more thermally labile nitramines and nitrate esters.

We calculated recoveries from the higher spikes (Fig. 5) for those analytes that had MDL less than



b) AEC soil, 5 µg/kg.



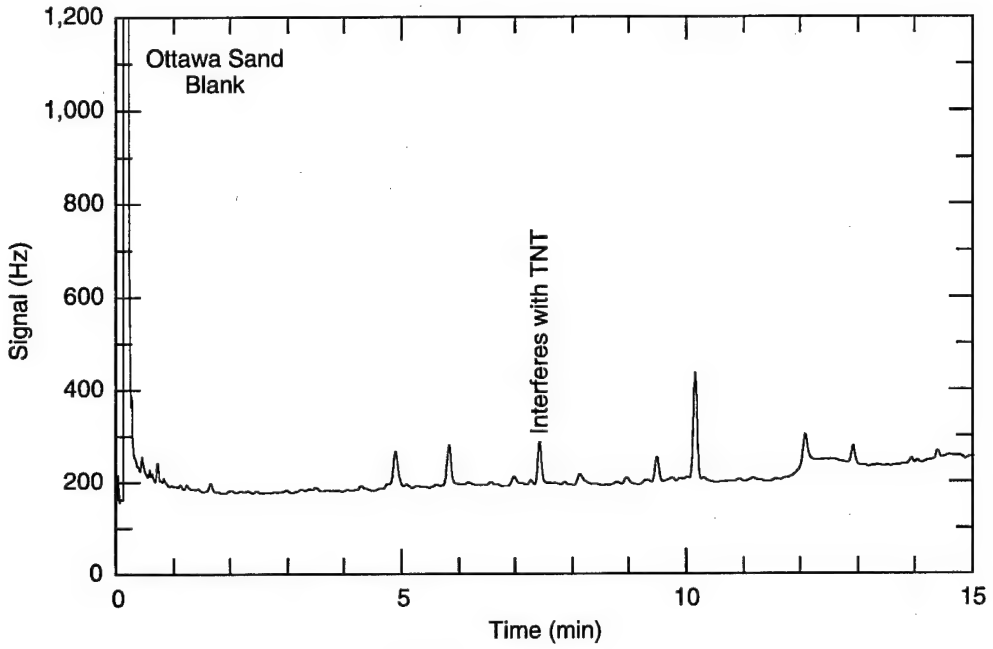
c) AEC soil, 50 µg/kg.

Figure 5 (cont'd).

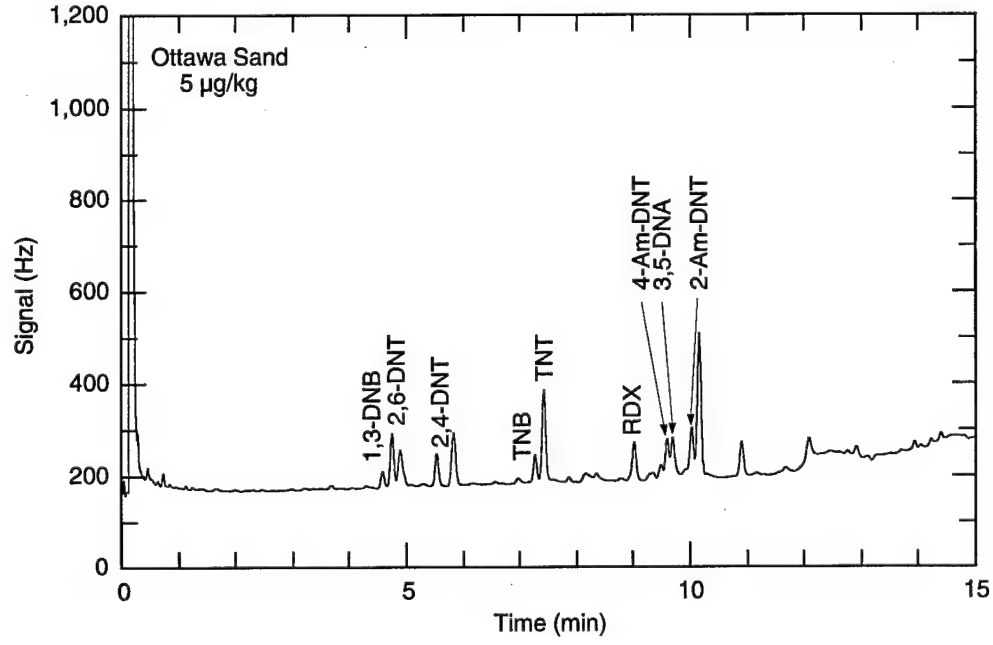
5 µg/kg (Table A5). In all cases, recoveries were near 100%. Precision was best (<4% RSD) for 1,3-DNB, TNT, and the DNT isomers.

NG and PETN were not degraded during the extended (18-hour) sonication in a cooled sonic bath (Table A6). Previously in our lab, we had observed a decrease in recovery of NG in spiked soils (2500 µg/kg) beyond two hours of sonication. However, the bath at that time was not cooled. Further kinetic studies with field-contaminated soils are needed to verify that 18 hours of sonication in a cooled sonic bath is not too long for acceptable recoveries of NG.

Using spiked matrices to determine precision

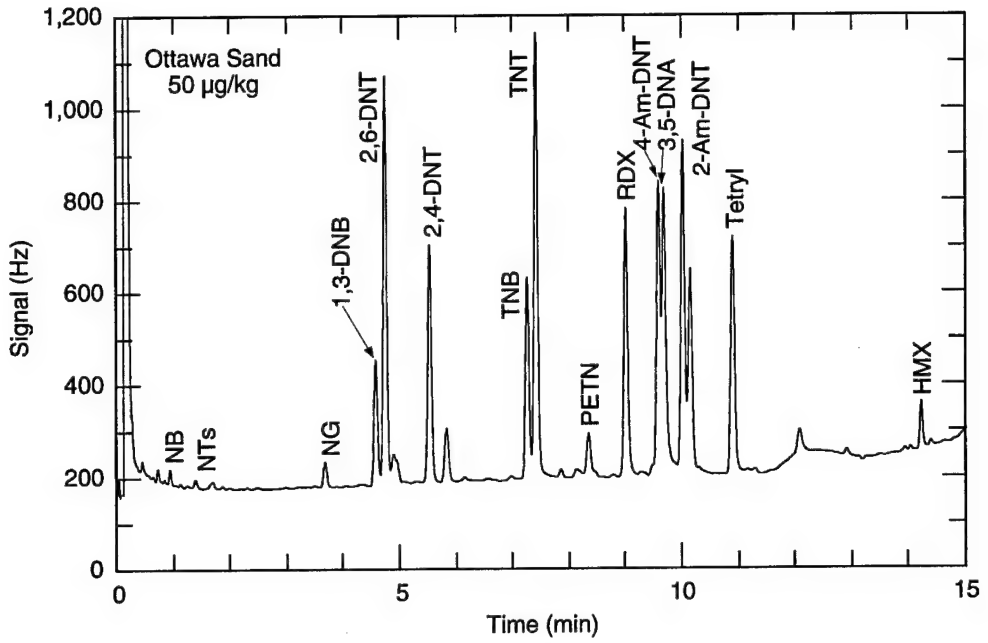


d) Ottawa sand, blank.



e) Ottawa sand, 5 µg/kg.

Figure 5 (cont'd). GC-ECD chromatograms of blank and spiked soils used for determination of method detection limits and spike recovery.



f) Ottawa sand, 50 µg/kg.

Figure 5 (cont'd).

Table 2. Method detection limits (µg/kg) of nitroaromatic, nitramine, and nitrate esters in spiked soils determined by GC-ECD.

	AEC soil	*Ottawa sand*	
	Method 1	*Method 1*	*Method 2*
1,3-DNB	0.93	0.73	1.2
1,4-DNB			0.86
1,2-DNB			0.64
2,6-DNT	0.81	0.69	
2,4-DNT	0.88	0.69	0.86
TNB	4.91	1.6	
TNT	0.45	2.4*	11*
RDX	3.1	3.4	2.6
4-Am-DNT	1.6	1.5	0.70
3,5-DNA	2.0	2.1	
2-Am-DNT	3.1	2.0	0.84
NB	14	17	
o-NT	12	12	
m-NT	11	11	
p-NT	9.5	10	
NG	31	13	
PETN	35	16	
Tetryl	66†	20	
HMX	26	25	

Method 1: 2 g soil extracted with 10 mL acetonitrile.
Method 2. 25 g soil extracted with 50 mL acetonitrile.
*Ottawa sand contained an interference that co-eluted with TNT.
†AEC soil contained an interference that co-eluted with tetryl.

and accuracy of an analytical method can produce confounding results because of the differing analyte stability in newly spiked versus field-contaminated aged soils (Grant et al. 1995). This difference became apparent when we spiked 25-g soil aliquots with the analytes of interest for mine detection (Table 1). The first soil we spiked was a silt obtained locally. As stated above, we added 1 mL of spike solution to 25 g of soil to yield a bulk analyte concentration of 2 µg/kg. However, this small volume of spike solution wetted only a small portion of the soil, unlike when we spiked 2-g soil aliquots. When we extracted the silt with acetonitrile containing 25 µg/L 3,4-DNT, recovery of all analytes was nil. The peak height for 3,4-DNT, the internal standard present throughout the extraction process, was normal, thus the loss of the spiked analytes must have occurred during the one hour of aging between the addition of the spike solution and the extraction solvent. To determine whether the loss was matrix-specific, we spiked duplicate 25-g samples of the following: glass beads (25-micron), Ottawa sand, AEC soil, and the same silt where loss was observed initially. Each matrix had interferences that co-eluted with at least one analyte, but we found that recovery bracketed 100% for analytes spiked onto the glass beads and the Ottawa sand, bracketed 90% for one replicate of the AEC soil and 50% for the other rep-

licate, and was nil again for the silt. We next spiked 10 replicates of Ottawa sand to obtain an estimate of MDL (Table 2, Table A7) for extraction of 25 g of soil with 50 mL of acetonitrile, and we found that the MDL were very similar to those obtained using just 2 g of soil and 10 mL of acetonitrile. The expectation of improvement in detection capability by using more soil in proportion to the volume of extraction solvent was negated by the small interfering peaks introduced by the matrix.

To further explore matrix effects on analyte recovery, we spiked 5 replicate 25-g samples of Ottawa sand with 5 mL of spike solution to yield 10-µg/kg nitroaromatic and 40-µg/kg RDX concentrations. We used a larger volume of spike solution to wet as much soil as possible, and we allowed the spiked samples to age uncapped in the fume hood for 24 hours. Recoveries were around 80% for the nitroaromatics (except TNT due to co-elution of an unknown interference) and 90% for RDX (Table A8).

Next we spiked five replicate samples of AEC soil, silt, and wet silt (5 mL of water added to 25 g of silt) using the same procedure as for sand. We also added spike solution to two empty test tubes and left the tubes uncapped for 24 hours, as for the tubes containing the spiked soils. Recoveries were around 90% for the samples without soil, but were inconsistent and low from each of the spiked soils (Table A9), showing that these soils are either actively sequestering or destroying the analytes added at such a low concentration (10 µg/kg). The AEC soil has been used many times before for spike recovery studies that used HPLC analysis, and several years ago it was used to examine the stability of spiked soils (Bauer et al. 1989). In this study 2-g soil samples were spiked with 1 mL of spike solution to yield a target concentration of 4000 µg/kg, the solvent was allowed to evaporate, and the spiked soils were stable for up to 62 days. Now, when we use a small volume of spike solution in proportion to the amount of soil spiked, and spike at a much lower concentration (10 µg/kg), the soil matrix effects on spiked analytes become pronounced, resulting in low and inconsistent recoveries of the spiked analytes from some matrices.

Looking back on the MS/MSD of field-contaminated soils (Table A2), we note variable recoveries. Lacking extensive characterization of each of these soils, the cause of the variable recoveries is open to speculation. One difference that was visually obvious was grain size. The finest-grained soil was that from Chickasaw, and this soil did show poor recovery (41 to 74%) of the spiked analytes. However, grain size alone did not account for low recovery in one of the Fort Ord samples, each of which was sandy. The reason for the difference in stability of spiked versus aged, field-introduced analytes is beyond the scope of this study, but this difference greatly reduces our ability to judge method accuracy.

Drying of samples

More artifacts associated with spiking were revealed when we attempted to fortify soils with analytes from the vapor phase. We wanted to know whether soil samples collected from a minefield should be extracted field-moist to prevent loss of the more volatile analytes. Air-drying is desirable because it facilitates homogenization and prevents introduction of water into the gas chromatograph where it can degrade the deactivated injection port liner.

In the first experiment, we placed 50 g of AEC standard soil in a porous nylon bag and suspended the bag above crystals (1 g) of TNT (Kodak). We wetted another 50 g of AEC soil with 10 mL of distilled water, and placed the damp soil in another nylon bag and suspended it over another 1 g of TNT. In both cases, the soil and TNT were sealed in 1-gallon glass jars for one week in the dark. A shallow dish of distilled water was added to the jar containing the damp soil to prevent the soil from drying during exposure to the TNT vapor.

The analytes found in the TNT vapor were determined by headspace solid-phase micro extraction (SPME) (polyacrylate) (Jenkins et al. [in prep]). Major peaks in the chromatogram for which we had standards were (in decreasing order) 2,4-DNT, 3,5-DNT, 2,5-DNT, 1,3-DNB, 2,3-DNT, 2,6-DNT, 2,4,6-TNT, 1,2-DNB, and 3,4-DNT.

After one week of exposing the soils to the TNT vapor, each soil was split by fractional shoveling. Five replicate 2-g subsamples were taken from half of each soil sample and each subsample placed immediately in 10 mL of acetonitrile. The other half of each soil was spread on an aluminum pie pan and placed in a fume hood overnight. The next morning, five replicate 2-g subsamples were taken from each air-dried soil and each subsample placed in 10 mL of acetonitrile. All samples were sonicated overnight, then filtered and analyzed by GC-ECD.

Analytes found in the soil (Table 3) that was not wetted were the same as those found in the vapor, in roughly the same order of abundance,

Table 3. Concentrations of analytes found in dry and moist AEC soil exposed at room temperature for one week to vapor from Kodak TNT.

	Soil concentration (μg/g)			
	Dry		*Initially moist*	
	*Not air-dried**	*Air-dried†*	*Not air-dried*	*Air-dried*
2,4-DNT	1.34	1.13	0.57	0.55
	1.35	1.23	0.59	0.56
	1.36	1.24	0.60	0.61
	1.42	1.25	0.69	0.62
	1.58	1.26	0.79	0.67
Mean	1.41	1.22	0.65	0.60
Std. dev.	0.10	0.05	0.09	0.05
% loss		13%		not sig.
t stat		3.73**		0.98
2,4,6-TNT	0.13	0.10	0.010	0.011
	0.14	0.11	0.012	0.011
	0.16	0.12	0.013	0.012
	0.16	0.12	0.014	0.012
	0.17	0.14	0.018	0.014
Mean	0.15	0.12	0.013	0.012
Std. dev.	0.02	0.02	0.003	0.001
% loss		20%		not sig.
t stat		3.04**		0.96
1,3-DNB	0.093	0.082	0.022	0.021
	0.094	0.087	0.023	0.021
	0.095	0.087	0.024	0.024
	0.098	0.089	0.027	0.024
	0.11	0.090	0.030	0.026
Mean	0.098	0.087	0.025	0.023
Std. dev.	0.007	0.003	0.003	0.002
% loss		11%		not sig.
t stat		3.31**		1.10
2,6-DNT	0.027	0.022	0.010	0.0083
	0.028	0.023	0.010	0.0086
	0.028	0.024	0.011	0.0095
	0.029	0.024	0.012	0.010
	0.032	0.024	0.012	0.011
Mean	0.029	0.023	0.011	0.0093
Std. dev.	0.002	0.001	0.001	0.001
% loss		18%		16%
t stat		5.29**		2.60**
1,2-DNB	0.011	0.0080	not detected	
	0.011	0.0082	not detected	
	0.011	0.0086	not detected	
	0.012	0.0087	not detected	
	0.013	0.0087	not detected	
Mean	0.012	0.0084		
Std. dev.	0.0008	0.0003		
% loss		27%		
t stat		8.59**		

Table 3 *(cont'd)*. Concentrations of analytes found in dry and moist AEC soil exposed at room temperature for one week to vapor from Kodak TNT.

	Soil concentration (µg/g)			
	Dry		*Initially moist*	
	*Not air-dried**	*Air-dried†*	*Not air-dried*	*Air-dried*
2,5-DNT	0.088	0.076	0.0030	0.0029
	0.090	0.082	0.0031	0.0029
	0.090	0.082	0.0033	0.0032
	0.093	0.084	0.0035	0.0032
	0.106	0.085	0.0043	0.0035
Mean	0.093	0.082	0.0035	0.0031
Std. dev.	0.0074	0.0035	0.0005	0.0002
% loss		12%		not sig.
t stat		3.19**		1.34
2,3-DNT	0.078	0.064	0.013	0.010
	0.080	0.065	0.013	0.010
	0.080	0.068	0.013	0.011
	0.084	0.070	0.016	0.011
	0.092	0.070	0.017	0.012
Mean	0.0828	0.0672	0.014	0.011
Std. dev.	0.0059	0.0030	0.0020	0.0008
% loss		19%		24%
t stat		5.28**		3.60**
3,5-DNT	0.22	0.18	0.079	0.078
	0.22	0.20	0.081	0.079
	0.23	0.20	0.083	0.084
	0.24	0.20	0.089	0.085
	0.25	0.21	0.11	0.091
Mean	0.23	0.20	0.088	0.083
Std. dev.	0.015	0.009	0.011	0.005
% loss		13%		not sig.
t stat		3.88**		0.85
3,4-DNT	0.0081	0.0074	<d	<d
	0.0082	0.0075	<d	<d
	0.0084	0.0077	<d	<d
	0.0086	0.0078	<d	<d
	0.0096	0.0079	<d	<d
Mean	0.0086	0.0077		
Std. dev.	0.0006	0.0002		
% loss		11%		
t stat		3.24**		
4-Am-DNT	<d	<d	0.0073	0.0053
	<d	<d	0.0074	0.0054
	<d	<d	0.0077	0.0054
	<d	<d	0.0082	0.0068
	<d	<d	0.012	0.0072
Mean			0.008	0.006
Std. dev.			0.002	0.001
% loss				28%
t stat				2.66**

*Not air-dried: Five 2-g subsamples each of dry and moist soils placed in 10 mL acetonitrile immediately after removal from chamber containing TNT vapor.

†Air-dried: Five 2-g subsamples each from dry and initially moist soils that were spread on aluminum pans and exposed in a ventilated area for 20 hours. This treatment served to air-dry the initially moist soil.

**Mean concentrations from five replicates were compared using a *t*-test to determine if air-drying resulted in analyte loss. Critical value of *t* for one-tailed test (alpha = 0.05) is 1.86.

except for 2,4,6-TNT, which was enriched compared to the vapor. The analyte found at the highest concentration was 2,4-DNT. Samples collected immediately after removal from the vapor exposure chamber had a mean concentration of 1.41 ± 0.10 mg/g; samples from the soil air-dried in the fume hood overnight had a mean concentration of 1.22 ± 0.05 µg/g for 2,4-DNT, a decrease of 13%. Similarly, all of the other analytes decreased in concentration after 24 hours in the fume hood. One-tailed t-tests indicated that the means for each analyte before and after drying in the fume hood were significantly different at the 95% confidence level. Except for 1,2-DNB, losses were 20% or less for each analyte.

Results were different for the soil that was moist during exposure to the TNT vapor. Less analyte sorbed to the moist soil. Again, the analyte found at the highest concentration was 2,4-DNT (0.65 ± 0.09 µg/g); however, air-drying did not result in a significant loss (0.60 ± 0.05). Losses were not significant for 2,4-6-TNT, 1,3-DNB, 2,5-DNT, and 3,5-DNT as well. In addition to those analytes found in the vapor, 4-Am-DNT, the microbial reduction product of TNT, was also found in the moistened soil.

To determine whether these results were repeatable with a different kind of soil, we set up two more exposure chambers, this time with TNT from an actual land mine (PMA-1A) that was made in the former Yugoslavia and with soil from Fort Leonard Wood. The soils were allowed to equilibrate for 68 days in the chambers and allowed to dry 24 hours and 48 hours prior to analysis.

The vapor from the Yugoslavian TNT differed from the Kodak TNT in that 1,3-DNB was present at levels similar to 2,4-DNT. When we analyzed subsamples from the soil that was not wetted, we found 1,3 DNB at 1.43 ± 0.12 µg/g, whereas 2,4-DNT was 1.10 ± 0.11 µg/g and 2,4,6-TNT was 1.14 ± 0.25 µg/g. Other TNT impurities were detected in the soil as well (Table 4). When this soil was spread on an aluminum pan and placed in a fume hood for 24 and 48 hours, concentration decreases were significant for all analytes except for 1,2-DNB. For the soil that was moist during exposure to the TNT vapor, only two analytes were detectable in the soil: 2,4-DNT at 0.065 ± 0.005 µg/g and 2,4,6-TNT at 0.008 ± 0.003 µg/g. Air-drying in the fume hood did not result in significant loss for either analyte.

Initially, we were surprised at the dramatic differences in concentrations between the wetted and non-wetted Fort Leonard Wood soils. Either sorption was minimal or the biological activity was sufficient to microbially transform the analytes as soon as they dissolved in the aqueous layer in the soil. Neither isomer of amino-DNT was detectable in the moist soil. However, when we extracted and analyzed the moist nylon bag and soil that clung to the bag, 2,4,6-TNT, 4-Am-DNT, and 2-Am-DNT were major peaks in the chromatogram. Concentrations were 1.9, 2.2, and 1.4 µg/g, respectively. Based on these results, microbial transformation is significant in the Fort Leonard Wood soil. A recent estimation of the half-life of TNT in this Fort Leonard Wood soil confirms this conclusion (Miyares and Jenkins in prep).

Both the AEC and Fort Leonard Wood soils that were not wetted had significant loss of analyte when removed from the vapor exposure chamber and air-dried in the fume hood. Because contamination of the soil was by adsorption from the vapor phase, some loss over a 24-hour period was expected because analytes will slowly desorb from soil exposed to flowing air. However, differences between analytes in the amount of loss are not explained by differences in partition coefficients, molecular weights, and vapor pressure. Compared to the isomers of DNB and DNT, TNT has a higher soil/air partition coefficient, a lower vapor pressure, and a higher molecular weight, leading to the prediction that desorption from the soil would be slower for TNT than the more volatile impurities. Another mechanism of loss, chemical or biological, may account for this artifact.

The presence of moisture in the soil had a dramatic effect on the amount of analyte we found in the soil. We expected lower concentrations in the moist soil than in the soil that was not wetted because of the aqueous boundary layer into which the analytes had to dissolve before partitioning onto the soil. However, the film of water apparently activated the microbial populations within the soils, and was thus not only a barrier to diffusion but also a site of transformation. The biological activity of the moist Fort Leonard Wood soil reduced the amount of analyte sorbed to below detection limits for analytes other than 2,4-DNT and 2,4,6-TNT. The small concentrations of these two analytes that we detected in the moist soil appeared to be unaffected by air-drying. Perhaps as the soil dries, the matrix collapses in such a way as to sequester the small amount of sorbed analytes.

This series of experiments failed to answer our objective of determining the effect of air-drying on the more volatile analytes expected in minefield

Table 4. Concentrations of analytes found in dry and moist Fort Leonard Wood soil exposed at room temperature for 68 days to vapor from Yugoslavian TNT.

	Soil concentration (μg/g)					
	Dry			*Initially moist*		
	Not air-dried	*Air-dried 24 hrs.*	*Air-dried 48 hrs.*	*Not air-dried*	*Air-dried 24 hrs.*	*Air-dried 48 hrs.*
2,4-DNT	0.96	0.82	0.71	0.061	0.052	0.060
	1.07	0.85	0.77	0.062	0.055	0.061
	1.07	0.91	0.78	0.064	0.062	0.063
	1.13	0.92	0.89	0.067	0.071	0.064
	1.27	0.96	1.01	0.074	0.075	0.072
Mean	*1.10*	*0.89*	*0.83*	*0.065*	*0.063*	*0.064*
Std. dev.	0.11	0.06	0.12	0.005	0.010	0.005
% loss		19%	24%		not sig.	not sig.
2,4,6-TNT	0.89	0.49	0.53	0.005	0.006	0.009
	1.01	0.65	0.64	0.006	0.007	0.010
	1.07	0.71	0.66	0.007	0.008	0.011
	1.21	0.77	0.68	0.011	0.009	0.012
	1.53	0.86	0.78	0.011	0.009	0.012
Mean	*1.14*	*0.69*	*0.66*	*0.008*	*0.008*	*0.011*
Std. dev.	0.25	0.14	0.09	0.003	0.001	0.001
% loss		39%	42%		not sig.	not sig.
1,3-DNB	1.27	1.17	1.03	<d	<d	<d
	1.40	1.24	1.06	<d	<d	<d
	1.44	1.30	1.08	<d	<d	<d
	1.47	1.40	1.18	<d	<d	<d
	1.59	1.51	1.44	<d	<d	<d
Mean	*1.43*	*1.32*	*1.16*			
Std. dev.	0.12	0.14	0.17			
% loss		7.6%	19%			
1,2-DNB	0.145	0.128	0.122	<d	<d	<d
	0.145	0.128	0.124	<d	<d	<d
	0.147	0.145	0.126	<d	<d	<d
	0.149	0.148	0.130	<d	<d	<d
	0.155	0.169	0.156	<d	<d	<d
Mean	*0.15*	*0.14*	*0.13*			
Std. dev.	0.004	0.017	0.014			
% loss		not sig.	not sig.			
2,5-DNT	0.032	0.029	0.026	<d	<d	<d
	0.036	0.030	0.026	<d	<d	<d
	0.037	0.033	0.028	<d	<d	<d
	0.038	0.035	0.031	<d	<d	<d
	0.040	0.037	0.037	<d	<d	<d
Mean	*0.037*	*0.033*	*0.030*			
Std. dev.	0.003	0.003	0.004			
% loss		11%	19%			
3,5-DNT	0.182	0.153	0.130	<d	<d	<d
	0.191	0.155	0.140	<d	<d	<d
	0.204	0.161	0.142	<d	<d	<d
	0.214	0.169	0.168	<d	<d	<d
	0.244	0.175	0.186	<d	<d	<d
Mean	*0.21*	*0.16*	*0.15*			
Std. dev.	0.024	0.009	0.023			
% loss		21%	26%			

Table 4 (*cont'd*).

Soil concentration (µg/g)

	Dry			*Initially moist*		
	Not air-dried	*Air-dried 24 hrs.*	*Air-dried 48 hrs.*	*Not air-dried*	*Air-dried 24 hrs.*	*Air-dried 48 hrs.*
2,3,4-TNT	0.092	0.053	0.053	<d	<d	<d
	0.098	0.071	0.064	<d	<d	<d
	0.108	0.075	0.071	<d	<d	<d
	0.110	0.082	0.072	<d	<d	<d
	0.142	0.088	0.079	<d	<d	<d
Mean	0.110	0.074	0.068			
Std. dev.	0.019	0.013	0.010			
% loss		33%	38%			

samples. Rather, it proved yet again that spiking of soils to simulate field contamination can lead to more questions than are answered. During the subsequent months, we received three batches of soils from minefields, one from Sandia and two from Fort Leonard Wood. The soils from Sandia were very dry and not refrigerated. The first batch from Fort Leonard Wood was dry and the second batch had soils of various moisture contents. We took the conservative approach and extracted all soils as received.

Minefield samples

Sandia soils and salting-in preconcentration

Soils from Sandia were collected from an experimental minefield. Three sets of samples were collected, each set corresponding to a different buried object. The three objects were 1) a cotton swatch containing milligram quantities of TNT, DNT, and RDX covered in fiberglass netting; 2) a high-density polyethylene (HDPE) box about the size of an anti-tank mine, spray-painted with a mixture of TNT, DNT, and RDX at about 10^{-5} g/cm^2 with about 75 g of TNT, DNT, and RDX crystals inside the box; and 3) a TM-62P anti-tank mine (a plastic-cased mine containing 5.7 to 8.3 kg TNT [Department of Defense 1999]). Surface soils were collected directly above each object and 23 and 46 cm to the north for a total of nine samples.

When the soils were received in the laboratory, triplicate 2-g subsamples of each were weighed. One of the replicates was spiked with 1 mL of spike solution to yield 50 µg/kg of 1,4-DNB, 1,3-DNB, 1,2-DNB, 2,4-DNT, TNT, 4-Am-DNT, and 2-Am-DNT; the spiked samples were aged 60 minutes prior to extraction. The other two replicates were extracted with 10 mL of acetonitrile. Also, duplicate 25-g aliquots of soils were extracted with 50 mL of acetonitrile. Following sonication overnight, samples were filtered and analyzed by GC-ECD using the HP-5 separation.

Explosives were detected in only those samples directly above the objects, and with the exception of RDX above the first object, were close to detection limits (Table 5). Mean recoveries for the seven spiked analytes from the nine matrix spike samples were 106 ± 7%.

Because the concentrations of the nitroaromatic analytes in the unspiked samples were so low, we tested the feasibility of using salting-in preconcentration (Jenkins and Miyares 1991). For each object, we preconcentrated the acetonitrile from one replicate 25-g sample that was extracted with 50 mL of acetonitrile (Table 5). In a 250-mL glass volumetric flask, 65 g of NaCl (Morton) were dissolved into 200 mL of reagent-grade water by stirring with a magnetic stirrer. Once all the salt was dissolved, we added 40 mL of acetonitrile soil extract. All of the acetonitrile dissolved into the salt water in two out of the three samples. An additional 3 mL of acetonitrile was added and stirring continued. The stirring was stopped and the phases allowed to separate. Then the acetonitrile layer (around 3.5 mL) was removed with a glass Pasteur pipet. 3,4-DNT was added as an internal standard (1 µL of a 200 mg/L solution in acetonitrile). This procedure will result in some deposition of salt in the injection port liner, and we were concerned that after multiple injections this deposition would reduce precision. To determine whether this concern was justified, additional

Table 5. Analytes detected in soils collected above three objects in an experimental minefield at Sandia National Laboratory.

	Soil concentration (µg/kg)				
Analyte	*2 g:10 mL Rep 1*	*2 g:10 mL Rep 2*	*25 g:50 mL Rep 1*	*25 g:50 mL Rep 2*	*Salted-in*
Cotton swatch: mg quantities of TNT, DNT, and RDX covered in fiberglass window screen netting					
TNT	3.52	3.65	2.85	4.52	1.90
RDX	60.6	48.3	38.2	61.5	33.2
4-Am-DNT	0.95	0.95	0.38	0.38	5.3
2-Am-DNT	11.4	8.82	6.89	12.6	14.0
Surrogate S-5: HDPE box about the size of anti-tank mine, spray-painted with a mixture of TNT, DNT, and RDX and containing 75 g of TNT, DNT, and RDX crystals					
2,4-DNT	1.55	0.74	0.89	1.49	1.2
TNT	1.94	1.76	0.62	1.63	0.71
RDX	<d	<d	1.47	2.90	1.5
2-Am-DNT	1.07	0.70	0.29	0.64	<d
Land mine AT-3, Bakelite TM62P anti-tank					
TNT	1.53	0.96	0.93	1.11	0.67
2-Am-DNT	0.90	<d	<d	<d	<d

samples were preconcentrated and analyzed six times each. These were duplicate 50-mL aliquots of a 5-µg/L solution containing the Method 8330 analytes plus NG, PETN, and 3,5-DNA. We also preconcentrated blank acetonitrile to test for interfering peaks.

The salted-in soil extracts, preconcentrated by a factor of 11, yielded concentrations generally consistent with what we found in the unconcentrated extracts (Table 5). The salting-in procedure did not introduce interfering peaks, nor did we see a change in responses for the analytes. The relative standard deviation for six injections of the preconcentrated standard solutions ranged from a low of 1.1% for NG to a high of 10% for RDX, and were generally around 5%. Following these analyses, the injection port liner was removed, and white, presumably salt, residue was visible in the liner. With frequent injections of check standards, the salting-in procedure appears to be a viable option for preconcentrating samples prior to GC-ECD.

Aside from providing a sufficient volume of solvent for preconcentration, extraction of 25-g soil samples with 50 mL of solvent did not enhance detection capability (Table 5) over the standard 2-g soil samples with 10 mL of solvent.

Fort Leonard Wood soils

The next sets of soils we received were collected from an experimental minefield at Fort Leonard Wood where various defused anti-tank and anti-personnel mines are buried. The mines were manufactured in the former Yugoslavia and each contained TNT (0.1–0.2 kg in anti-personnel mines and 5.5–5.6 kg in anti-tank mines). The first set of soil samples was collected two months after the mines were buried and revealed which analytes are actually present in soils surrounding emplaced land mines. Of the 143 samples we received, only 28 had detectable analytes (Table 6) as determined by GC-ECD with confirmation by HPLC-UV. The most common analytes detected were 2,4-DNT, 4-Am-DNT, and 2-Am-DNT, each of which was found in 27 out of the 28 positive samples and each at median concentrations greater than 60 µg/kg. 2,4,6-TNT was found in 24 samples and tended to be lower in concentration than the Am-DNTs, indicating that it is undergoing microbiological transformation. Median 2,4,6-TNT concentration was 6.5 µg/kg, and the maximum was over 3000 µg/kg in a soil collected next to a mine. The other two commonly found analytes were 1,3-DNB and 2,6-DNT, which had median concentrations of 8.8 and 3.1 µg/kg, respectively. Agreement between duplicates was similar to that observed previously for these analytes (Table 6).

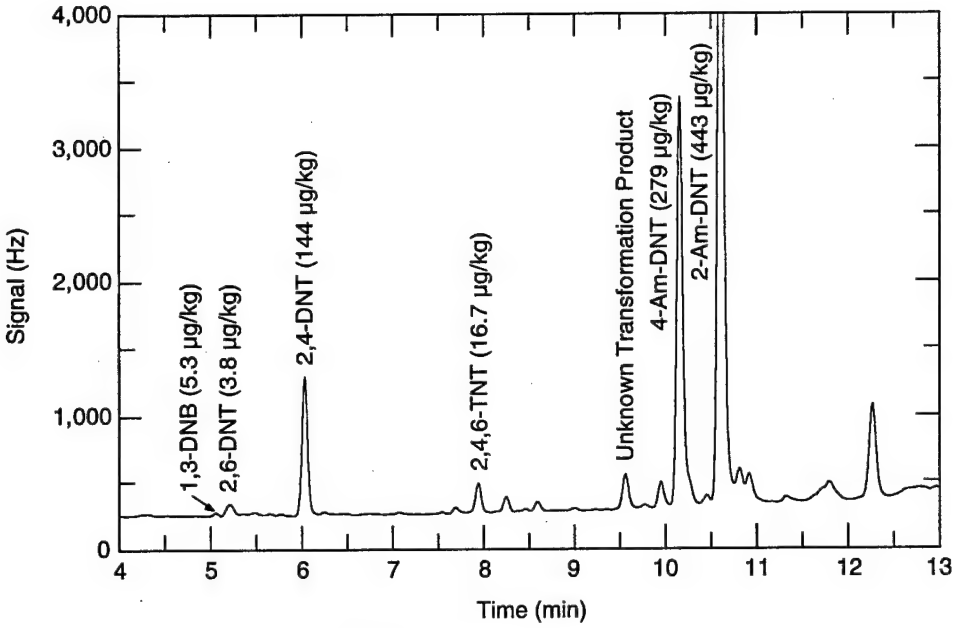
More soils were collected four months after the mines were buried; out of 199 samples, 73 had detectable explosives. Figure 6 shows chromato-

Table 6. Most common analytes detected in soils collected from an experimental minefield at Fort Leonard Wood two months after the mines were emplaced. The relative percent differences (%) are shown in parentheses for replicates.

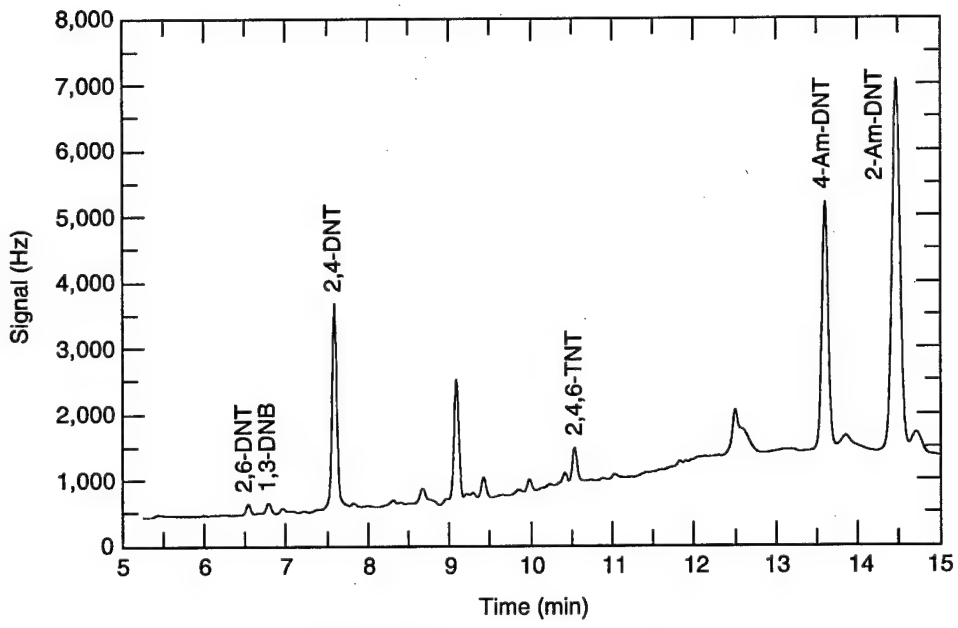
Lab sample #	*Mine type*	*Depth**	*Concentration (µg/kg)*					
			2,4-DNT	*2,4,6-TNT*	*2-Am-DNT*	*4-Am-DNT*	*1,3-DNB*	*2,6-DNT*
13	PMA1A	X	12	1.2	8.1	8.9	4.7	<d
13 rep			16 (29%)*	1.3 (14%)	9.7 (18%)	11 (18%)	5.4 (14%)	<d
32	PMA1A	S	<d	<d	198	166	<d	<d
30	PMA1A	T	77	1.5	314	317	32	1.1
29	PMA1A	X	11	1.5	29	21	4.0	<d
29 rep			18 (50%)	<d	40 (31%)	37 (53%)	6.8 (52%)	<d
124	TMA5	T2	2.3	<d	3.3	2.1	<d	<d
134	TMA5	X	116	3.9	164	115	3.9	0.7
134 rep			96 (19%)	10 (87%)	127 (25%)	86 (30%)	4.8 (19%)	<d
200	TMA5	S	3.9	<d	14.9	14.8	<d	<d
65	TMA5	T1	108	16	469	229	7.2	1.9
69	TMA5	T2	520	23	720	434	16	8.9
67	TMA5	X	2966	3267	2089	1642	131	46
67 rep			3505 (17%)	4270 (27%)	2692 (25%)	2760 (51%)	205 (44%)	39 (15%)
202	TMA5	S	29	3.7	90	70	<d	<d
66	TMA5	T1	61	4.7	94	52	1.0	<d
64	TMA5	T2	409	43	925	495	12	3.3
63	TMA5-22	X	271	20	511	454	8.1	3.1
63 rep			280	24	571	381	13	<d
2	TMA5	T1	15	3.2	25	24	1.7	<d
8	TMA5	T2	70	16	117	156	<d	<d
4	TMA53	X	317	44	474	324	8.8	1.7
4 rep			377 (18%)	61 (33%)	585 (21%)	425 (27%)	10 (17%)	<d
203	TMA5	S	60	5.2	17	13	<d	<d
10	TMA5	T1	20	2.2	48	35	<d	<d
6	TMA53	T2	21	4.0	36	28	1.3	<d
1	TMA5	X	89	7.7	77	59	3.5	<d
1 rep			71 (23%)	7.7 (1%)	60 (25%)	71 (20%)	<d	<d
108	TMA5	X	22	1.1	10	15	<d	<d
108 rep			38 (55%)	<d	17 (58%)	14. (7%)	<d	<d
120	TMA5	X2	437	46	144	115	35	4.3
120 rep			480 (9%)	51 (11%)	161 (11%)	240 (70%)	45 (26%)	4.4 (3.1%)
100	TMA5	X	28	<d	20	18	<d	<d
100 rep			35 (22%)	<d	24 (19%)	29 (44%)	<d	<d
114	TMA5	T2	66	42	40	66	23	1.2
117	TMA5	X2	201	250	88	102	106	<d
117 rep			204 (1%)	233 (7%)	84 (5%)	80 (25%)	93 (13%)	<d
20	PMA2	contact	1523	60	<d	<d	503	6.9
22	TMA5	contact	53	4	11	10	16	<d

*S: Surface soil.
T1: 2-cm-long core just under surface soil.
T2: Core of soil between T1 and X.
X: 2-cm-long core of soil just above the center of the mine's top surface.

grams obtained on the analytical and confirmation column of a soil containing the suite of frequently detected analytes. The amino-DNTs were the most frequently detected analytes, with 71 detections of 2-Am-DNT and 61 detections of 4-Am-DNT. In previous comparisons we have made between GC-ECD and HPLC-UV, we have not had a sufficient number of samples with analytes at sufficiently high concentrations for determination by HPLC. For this data set, we compared concentration estimates over 100 µg/kg for the amino-DNTs and over 50 µg/kg for 2,4-DNT (Fig. 7). GC concentration estimates were obtained using an HP 6890 µ-ECD without dilution of the soils extracts. Correlation between the two methods for 2,4-DNT was similar to what we have previously



a) HP-5 analytical column.



b) RTX-225 confirmation column.

Figure 6. GC-ECD chromatograms of soil extracts from a minefield sample.

observed; the correlation coefficient was greater than 0.99 and the slope slightly greater than 1.00. Correlation coefficients were 0.951 and 0.956 for 2-Am-DNT and 4-Am-DNT, respectively. The slopes of the least squares regression lines were not significantly different from 1.00 for either analyte. The data are more scattered for these two analytes, showing that accurate determinations are more difficult to obtain than 2,4-DNT. Like the nitramines, the amino-DNTs are susceptible to degradation as the GC injection port liner becomes less and less inert with repeated injections of soil extracts. On the HPLC separation, these analytes elute late where the peaks are quite broad.

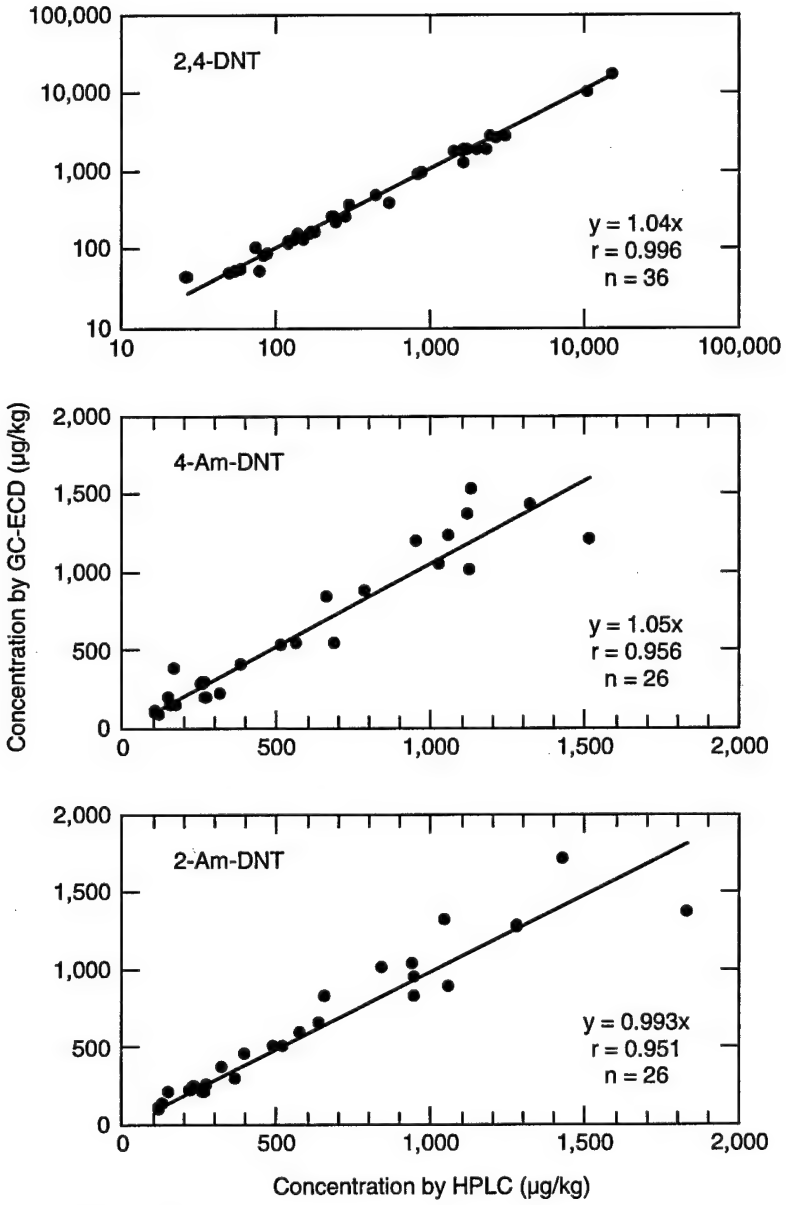


Figure 7. Correlation analysis of GC-ECD concentration (µg/kg) estimates with those from HPLC-UV analysis using splits of the same acetonitrile extracts from soils collected from an experimental minefield.

Similar to the first set of samples collected from this minefield, we detected 2,4,6-TNT generally at lower concentrations than the amino-DNTs, except for samples collected in contact with a mine. The presence of the TNT biotransformation products implies that 2,4-DNT and 1,3-DNB biotransformation products should be present as well. These products would be 2-amino-4-NT, 4-amino-2-NT, and 3-nitroaniline. Unfortunately, the ECD response is not strong for these compounds because they each have only one nitro group. However, the vapor pressure of these analytes might be sufficiently high to make them valuable markers for detection of emplaced mines. If other research shows that these analytes are important for mine detection, analytical methods would need to be optimized for these compounds. Salting-in preconcentration with HPLC-UV detection would be a viable approach.

In the second set of samples from Fort Leonard Wood, several very fine-grained wet soils were collected underneath a mine. Previously we ob-

Table 7. Comparison of concentration estimates obtained using small (2-g) soil subsamples to those obtained from large (20-g) subsamples.

	Sample N231		*Sample N236*		*Sample N214*		*Sample N240*		*Sample N202*	
Lab sample #	*2 g:5 mL*	*20 g:50 mL*	*2 g:5 mL*	*20 g:50 mL*	*2 g:5 mL*	*20 g:50 mL*	*2 g:5 mL*	*20 g:50 mL*	*2 g:5 mL*	*20 g:50 mL*
1,3-DNB	49.1	39.5	10.8	7.1	2.9	trace	<d	<d	<d	<d
2,4-DNT	2510	2630	1800	1650	156	152	110	349	3640	2760
TNT	383	491	77.3	53.4	3.6	8.7	45.3	6.0	1680	1460
4-Am-DNT	540	377	1030	838	87.6	109	60.3	184	1420	1190
2-Am-DNT	501	496	1030	819	88.1	104	65.9	198	1270	998
2,6-DNT	75.2	65.1	29.2	24.7	4.6	12.3	<d	7.1	54.5	45.8
2,5-DNT	11.8	13.8	1.8	<d	1.1	<d	<d	<d	25.7	23.0
3,5-DNT	147	205	156	150	8.5	trace	2.7	23	589	526
3,4-DNT	3.3	16.8	0.8	<d	<d	<d	<d	<d	33.2	8.9
3,5-DNA	<d	<d	<d	<d	<d	<d	<d	<d	144	99.3
TNB	27.5	38.6	14.7	<d	<d	<d	<d	12.3	194	154
3-NA	71.4	40.0	93.0	34.7	12.4	19.1	trace	20.1	123	94
2,4,5-TNT	1.1	<d	<d	<d	<d	<d	<d	<d	10.0	8.5
1,4-DNB	<d	<d	<d	<d	<d	<d	<d	<d	1.2	<d
4-Am-2-NT	133	86.3	157	80	<d	<d	<d	<d	<d	<d
2,3,4-TNT	4.4	<d	<d	<d	<d	<d	<d	<d	38	49
1,2-DNB	<d	<d	<d	<d	<d	<d	<d	<d	trace	trace
2-Am-4-NT	197	115	208	148	<d	<d	<d	<d	<d	<d

served that extraction of large samples did not enhance detection capability, but for these soils, which were difficult to homogenize, larger samples might be more representative. However, we did not see significant differences in the analytes detected for in the concentration estimates in four of the five samples extracted using 2-g and 20-g subsamples (Table 7). The additional solvent consumption required to extract larger samples is not justified for routine analysis, based on these results.

CONCLUSIONS

We compared GC-ECD concentration estimates of nitroaromatic and nitramines in field-contaminated soils with estimates obtained by the standard HPLC-UV method, and we found good correlation between the two methods of analysis. The GC-ECD provided improved chromatographic resolution and detection. We used two extraction procedures, both of which involved 18 hours of sonication in a cooled bath. In one method we extracted 2 g of soil with 10 mL of acetonitrile, and in the second we extracted 25 g of soil with 50 mL of acetonitrile. MDL were similar for these two methods because matrix interferences became more pronounced when the ratio of soil to solvent was increased from 1:5 to 1:2. MDL were around 1 µg/kg for the di- and trinitroaromatics, about 10 µg/kg for the mononitroaromatics, 3 µg/kg for RDX, 25 µg/kg for HMX, and between 10 and 40 µg/kg for the nitrate esters (NG and PETN).

Spike recovery studies revealed artifacts introduced when the mass of the soil spiked was large (25 g) in proportion to the volume of spike solution added (1 mL). Recoveries were excellent (around 100%) when 2-g soil samples were spiked with 1 mL of solution. However, when 25-g soil samples were spiked with 5 mL of solution, recoveries varied from nil in a silt to around 80% in a sand. MS/MSD of field-contaminated soils also showed inconsistency in recovery of the spiked analytes.

Additional experiments using vapor to spike dry and moistened soils revealed the transient nature of some of these analytes when introduced into soil. Results of these experiments led us to extract field-moist samples from a minefield to hasten sample preparation and eliminate the possibility of losses during drying.

Soils collected near emplaced mines contained various microbial transformation products of TNT, 2,4-DNT, and 1,3-DNB. The importance of these transformation products for land mine detection is uncertain at present.

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APPENDIX A: DATA.

Table A1. HPLC and GC concentration estimates (mg/kg) for field-contaminated soils using the Method 8330 extraction procedure (2 g soil:10 mL acetonitrile).

a) TNT

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
1	Iowa AAP	15350	9398	11370
2	Milan	35	18	23
3	NOP	2809	2660	2824
4	NOP	297	238	354
5	NOP	4.0	3.3	2.7
6	NOP	4.4	5.6	3.8
7	NOP	0.33	0.34	0.37
8	ERF	0.5	0.28	0.18
9	Monite	37500	27104	39014
16	NOP	139	66.4	89
17	Raritan	745	10921	10467
18	CFB	21	49	64
19	CFB	7.7	20	13
20	CFB	1.3	1.5	0.03
21	Savanna	14	12	9.7
22	Savanna	17	13	16
23	Savanna	4	3.09	2.8
24	Savanna	120	109	144

b) RDX

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
1	Iowa AAP	13900	13185	16304
2	Milan	465	350	400
3	NOP	104	685	920
4	NOP	803	651	859
5	NOP	19	19	25
6	NOP	986	869	1088
16	NOP	241	53	71
18	CFB*	not reported	0.28	0.32
19	CFB*	not reported	0.33	0.34
21	Savanna*	not reported	0.33	0.07
24	Savanna*	not reported	0.50	0.28

*Less than HPLC reporting limit.

c) 2,4-DNT

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
2	Milan	not reported	1.0	1.3
3	NOP	2.66	2.7	3.6
5	NOP	3.21	2.9	3.3
7	NOP	0.2	0.29	0.38
8	ERF*	27	0.09	0.86
9	Monite	not reported	83	20
10	Monite	11300	95062	119659
11	Monite	47000	24249	26436
12	Monite	3450	3264	3444
16	NOP	4.4	1.6	1.7
17	Raritan	43	24.0	27
18	CFB*	not reported	0.07	0.16
19	CFB*	not reported	0.07	0.20
22	Savanna	0.6	0.42	0.51
24	Savanna	not reported	4.57	5.07

*Less than HPL reporting limit.

Table A1 *(cont'd)*. HPLC and GC concentration estimates (mg/kg) for field-contaminated soils using the Method 8330 extraction procedure (2 g soil:10 mL acetonitrile).

d) TNB

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
1	Iowa AAP	550	569	487
2	Milan	2.5	1.9	0.38
3	NOP	14.5	184	75
4	NOP	100	83	64
5	NOP	71.1	60	8.1
6	NOP	0.94	2.0	0.04
7	NOP*	not reported	0.17	0.10
9	Monite	107	68	101
13	Mead	not reported	20	9.4
14	Mead	not reported	4.1	8.5
16	NOP	143	59	17.2
17	Raritan	3.9	8.1	5.0
18	CFB	not reported	0.38	0.26
19	CFB*	not reported	0.23	0.25
20	CFB*	not reported	0.15	3.4
21	Savanna	9.4	15	4.8
22	Savanna	0.46	0.49	0.65
23	Savanna	1.6	1.6	1.0
24	Savanna	2.2	1.96	1.1

*Less than HPLC reporting limit.

e) DNB

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
1	Iowa AAP	45	13	17
2	Milan	0.86	0.60	0.34
3	NOP	2.2	4.8	5.0
4	NOP	2.2	3.3	4.5
10	Monite	not reported	314	348
11	Monite	not reported	325	318
12	Monite	not reported	49	50
16	NOP	1.9	1.1	1.3
17	Raritan	not reported	5.3	4.7
21	Savanna	0.2	0.43	0.04
23	Savanna*	0.05	0.05	0.03
24	Savanna	1.3	1.2	1.5

*Less than HPLC reporting limit.

f) HMX

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
1	Iowa AAP	2000	2018	1301
2	Milan	86	70	29
3	NOP	12	110	310
4	NOP	82	83	40
5	NOP	3.3	3.5	1.3
6	NOP	93	108	172
16	NOP	21	18	5.4
18	CFB	800	780	482
19	CFB	360	416	347
20	CFB	600	717	448

Table A1 *(cont'd).*

g) 4-Am-DNT

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
6	NOP	1.6	1.6	1.1
17	Raritan	not reported	23	23
18	CFB	3.6	3.1	1.5
19	CFB	0.9	1.9	0.93
22	Savanna	not reported	10	6.0
2	Milan	not reported	not resolved	1.2

h) 2-Am-DNT

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
2	Milan	not reported	1.1	0.93
5	NOP	0.18	0.14	0.26
8	ERF	0.5	0.23	1.1
3	NOP	2.7	not resolved	1.9
17	Raritan	37	not resolved	25
18	CFB	2	not resolved	1.2
22	Savanna	8	not resolved	3.5

i) 3,5-DNA

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
2	Milan	not reported	0.53	0.48
3	NOP	not reported	3.1	3.4
4	NOP	not reported	4.4	5.4
5	NOP	not reported	0.70	0.20
21	Savanna	not reported	0.11	0.16

j) Tetryl

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
1	Iowa AAP	330	136	207
2	Milan	34.7	0.75	1.1
6	NOP	not reported	1.4	0.04
13	Mead	397	277	79
14	Mead	60	36	8.7
15	Mead	1265	1062	899
16	NOP	not reported	0.34	0.36

k) 2,6-DNT

Soil ref. number	*Source*	*Previous HPLC*	*HPLC*	*GC*
2	Milan	not reported	1.0	0.39
3	NOP	not reported	2.6	1.6
4	NOP	not reported	1.8	7.5
10	Monite	not reported	25226	38781
11	Monite	not reported	18828	19270
12	Monite	not reported	2687	2580
16	NOP	not reported	5.1	0.39
21	Savanna	0.3	0.89	0.04
9	Monite	not reported	not resolved	14
17	Raritan	not reported	not resolved	2.9

NOTE: 2,6-DNT, 2,4-DNT, and 1,3-DNB concentration estimates obtained using alternative HPLC separation (Burdick and Jackson).

Table A2. GC concentration estimates (µg/kg) for field-contaminated soils and matrix spikes/ matrix spike duplicates (MS/MSD). 25-g soil subsamples were extracted with 50 mL of acetonitrile. Spiked concentration was 10 µg/kg for the nitroaromatics and 40 µg/kg for RDX.

Analyte	*1,4-DNB*	*1,3-DNB*	*1,2-DNB*	*2,4-DNT*	*TNT*	*RDX*	*4-Am-DNT*	*2-Am-DNT*
Eagle River Flats OB/OD Pad								
Rep 1	<d	<d	<d	36.2	42.9	40.5	27.7	21.1
Rep 2	<d	<d	<d	8587	23.9	48.9	29.0	26.9
Savanna AD RCF002D								
Rep 1	<d	<d	<d	24.7	149	13.6	155	159
Rep 2	<d	<d	<d	21.1	182	15.9	154	156
MS	9.3	12.2	12.9	34.6	191	46.8	176	179
MSD	8.9	11.3	14.0	29.0	185	51.5	162	174
Chickasaw (CRREL #15)								
Rep 1	<d	<d	<d	140	13.2	<d	1.7	1.4
Rep 2	<d	<d	<d	148	14.0	<d	1.5	1.4
MS	5.8	7.4	*	112	18.0	22.9	6.1	6.7
MSD	4.1	5.5	*	176	15.1	14.7	4.6	4.3
Nebraska Ord. Plant (CRREL 33)								
Rep 1	<d	<d	<d	<d	4.2	11.2	3.2	1.2
Rep 2	<d	<d	<d	0.96	4.7	5.6	2.0	0.85
MS	9.0	11.4	10.3	14.3	60.4	80.0	24.6	15.6
MSD	3.6	5.0	4.4	5.1	10.6	18.1	5.9	3.8
Nebraska Ord. Plant (CRREL 38)								
Rep 1	<d	3.41	<d	95.2	124	8.7	23.5	14.9
Rep 2	<d	6.85	<d	212	273	17.9	46.5	32.7
US Naval AD (#12728)								
Rep 1	<d	<d	<d	0.99	1.8	3.6	<d	<d
Rep 2	<d	<d	<d	1.24	2.0	3.5	<d	<d
MS	9.1	11.6	11.0	11.3	11.1	27.0	7.9	8.5
MSD	9.2	11.6	10.9	11.1	11.4	29.0	8.2	9.0
US Naval AD (#12731)								
Rep 1	<d	5.6	<d	<d	1.6	<d	<d	<d
Rep 2	<d	6.0	<d	<d	2.7	<d	<d	<d
MS	8.7	12.9	10.1	10.5	11.5	30.3	7.8	8.6
MSD	8.7	13.1	10.2	10.6	10.2	29.1	7.4	8.5

*Large peak corresponding to 2,6-DNT interfered with determination of 1,2-DNB.

Table A2 *(cont'd).*

Analyte	*1,4-DNB*	*1,3-DNB*	*1,2-DNB*	*2,4-DNT*	*TNT*	*RDX*	*4-Am-DNT*	*2-Am-DNT*
Camp Shelby NE Quad Pt. 2 (#15363)								
Rep 1	<d	<d	<d	145	1.3	23.6	<d	<d
Rep 2	<d	<d	*	4096	28.8	42.8	<d	<d
MS	13.3	15.8	*	2646	26.6	84.3	8.9	10.2
MSD	6.8	8.1	7.4	17.4	7.7	217	5.7	6.6
Fort Ord 2-48-1 15 to 30 cm								
Rep 1	<d	<d	<d	1.18	7.3	<d	30.1	66.3
Rep 2	<d	<d	<d	1.23	7.3	<d	30.6	66.0
MS	9.0	9.7	10.9	10.6	18.4	31.4	41.8	88.9
MSD	8.8	9.7	10.6	10.4	18.5	33.1	40.5	83.5
Fort Ord 2-48-1 30 to 45 cm								
Rep 1	<d	<d	<d	<d	4.6	<d	21.0	50.7
Rep 2	<d	<d	<d	0.94	8.8	<d	13.0	30.6
MS	4.3	5.0	5.2	5.0	11.3	15.0	22.3	58.6
MSD	5.9	6.4	7.2	6.7	22.6	21.6	18.7	40.3
Fort Ord 2-48-2 0 to 15 cm								
Rep 1	<d	<d	<d	1.6	11.6	<d	75.7	182
Rep 2	<d	<d	<d	1.6	11.7	1.3	77.0	187
MS	7.4	8.4	9.7	9.6	16.8	30.4	64.4	159
MSD	8.8	10.5	11.6	11.8	22.1	33.3	88.1	216
Fort Ord 2-48-2 15 to 30 cm								
Rep 1	<d	<d	<d	1.0	7.6	<d	40.3	89.1
Rep 2	<d	<d	<d	1.1	7.6	<d	41.2	92.9
MS	8.4	9.5	10.0	9.8	16.7	30.8	43.7	96.1
MSD	8.9	9.9	10.7	10.4	17.8	36.8	42.5	95.9
Fort Ord 2-48-5 15 to 30 cm								
Rep 1	<d	<d	<d	<d	6.5	<d	55.1	136
Rep 2	<d	<d	<d	<d	7.1	<d	58.2	144
MS	9.4	10.8	11.6	11.1	13.9	33.6	67.2	170
MSD	7.8	9.0	9.7	9.0	12.1	30.8	48.8	125

*Large peak corresponding to 2,6-DNT interfered with determination of 1,2-DNB.

Table A3. Retention times (min) on analytical and confirmation columns.

	Retention time (min)			
Analyte	*HP-5*	*RTX-225*	*RTX-200**	*RTX-200†*
NB	1.16	1.07		2.69
o-NT	1.74	1.46		3.41
m-NT	2.13	1.87		4.04
p-NT	2.32	2.19		4.34
NG	4.14	5.17		7.75
1,4-DNB	4.87	6.6	9.79	7.78
1,3-DNB	5.10	6.92	10.52	8.16
2,6-DNT	5.27	6.53	9.94	7.83
1,2-DNB	5.33	7.84	11.49	8.71
m-Nitroaniline	5.48	8.32		7.68
2,5-DNT	5.69	7.04		8.43
2,4-Dinitrophenol	5.69			8.39
tri-Nitroso-RDX	5.73			
2-Amino-6-NT	5.91	8.23		8.04
2,3-DNT	6.00	7.96		9.22
2,4-DNT	6.05	7.58	12.17	9.05
4-Amino-2-NT	6.17	8.51		8.2
3,5-DNT	6.28	7.84		9.46
3,4-DNT	6.68	9.00	14.39	10.25
2-Amino-4-NT	6.76	9.24		9.04
di-Nitroso-RDX	7.30			
TNB	7.79	11.13	17.01	11.52
2,4,6-TNT	7.95	10.61	16.5	11.25
mono-Nitroso-RDX	8.45			
PETN	8.85	7.23		13.00
2,4,5-TNT	8.86			12.53
2,3,4-TNT	9.12			12.93
RDX	9.55	15.06	20.84	13.38
3,4,5-TNT	9.69			13.87
2,4-Diamino-6-NT	9.77	13.78		12.2
TAX	10.11			
4-Am-DNT	10.15	13.86	18.98	12.54
3,5-Dinitrophenol	10.18			11.73
3,5-DNA	10.24	14.63	19.87	13.00
2,6-Diamino-4-NT	10.48	14.65		12.97
2-Am-DNT	10.59	14.43	20.87	13.38
Tetryl	11.47		25.17	14.74
HMX	15.66			

HP-5: oven program: 100°C for 2 min, to 250°C at 10°/min and held 3 min; injector 250°C; detector 280°C.
RTX-225: oven program: 100°C for 2 min, to 220°C at 10°/min and held 6 min; injector 220°C; detector 220°C.
*RTX-200: oven program: 100°C for 1 min, to 190°C at 5°C/min, to 200°C at 1°C/min, to 250°C at 20°C min.
†RTX-200: oven program: 100°C for 2 min, to 260°C at 10°/min and held 1 min; injector 250°C, detector 280°C.

Table A4. Found concentrations (µg/kg) and method detection limits determined from spiked soils (2 g soil:10 mL acetonitrile) after 18 hr of sonication.

a) Target concentration = 5 µg/kg

Rep	*1,3-DNB*	*2,6-DNT*	*2,4-DNT*	*TNB*	*TNT*	*RDX*	*4-Am-DNT*	*3,5-DNA*	*2-Am-DNT*
AEC soil									
1	5.0	4.9	5.1	5.6	5.9	5.8	6.2	6.6	8.2
2	4.6	4.5	4.7	9.6	5.8	4.6	4.9	5.4	7.1
3	5.3	5.1	5.3	6.7	5.9	5.9	5.6	6.3	8.1
4	5.2	5.1	5.3	7.3	6.0	6.2	5.9	6.5	7.8
5	5.3	5.2	5.3	6.3	6.0	5.9	5.6	6.2	8.2
6	5.4	5.2	5.4	8.9	6.2	6.9	5.9	6.8	10.1
7	5.4	5.3	5.5	5.6	6.1	7.7	6.5	7.5	9.3
Mean	5.2	5.0	5.2	7.1	6.0	6.1	5.8	6.5	8.4
Std. dev.	0.30	0.26	0.28	1.6	0.14	0.99	0.51	0.65	1.0
MDL	0.93	0.81	0.88	4.9	0.45	3.1	1.6	2.0	3.1
Ottawa sand									
1	5.8	5.5	5.8	12.3	10.3	10.4	6.5	7.9	7.5
2	5.9	5.5	5.9	12.3	10.7	9.5	6.6	7.9	7.7
3	5.2	4.9	5.3	11.1	8.5	7.8	5.5	6.4	6.1
4	5.6	5.4	5.7	11.9	9.0	8.0	6.2	7.5	7.1
5	5.6	5.5	5.7	12.1	9.6	9.4	6.5	7.5	7.3
6	5.8	5.5	5.8	11.3	9.3	7.6	5.4	6.3	6.2
7	5.6	5.5	5.7	11.3	9.9	9.7	6.4	7.6	7.2
Mean	5.6	5.4	5.7	11.8	9.6	8.9	6.2	7.3	7.0
Std. dev.	0.23	0.22	0.22	0.52	0.76	1.09	0.47	0.66	0.64
MDL	0.73	0.69	0.69	1.6	2.4	3.4	1.5	2.1	2.0

b) Target concentration = 50 µg/kg

Rep	*NB*	*o-NT*	*m-NT*	*p-NT*	*NG*	*PETN*	*Tetryl*	*HMX*
AEC soil								
1	43	45	62	53	57	63	56	47
2	42	46	57	51	54	61	42	36
3	47	50	61	54	57	60	41	44
4	46	52	63	52	32	34	48	23
5	49	52	64	55	52	57	37	42
6	48	51	63	55	51	56	33	31
7	56	56	69	60	64	70	95	35
Mean	47	50	63	54	53	57	50	37
Std. dev.	4.5	3.9	3.4	3.0	9.9	11	21	8.2
MDL	14	12	11	9.5	31	35	66	26
Ottawa sand								
1	37	50	56	43	64	66	96	80
2	46	54	55	46	59	59	88	62
3	49	57	54	36	66	68	102	78
4	37	50	49	41	62	62	95	79
5	49	58	53	43	64	63	94	78
6	46	58	54	39	72	74	107	86
7	48	57	47	39	61	61	93	67
Mean	45	55	53	41	64	65	96	76
Std. dev.	5.4	3.8	3.4	3.1	4.1	5.2	6.3	8.0
MDL	17	12	11	10	13	16	20	25

Table A5. Found concentrations (µg/kg) and recoveries determined from 2-g spiked soil samples extracted with 10 mL acetonitrile by 18 hr of sonication. Target concentration was 50 µg/kg.

Rep	*1,3-DNB*	*2,6-DNT*	*2,4-DNT*	*TNB*	*TNT*	*RDX*	*4-Am-DNT*	*3,5-DNA*	*2-Am-DNT*
AEC soil									
1	51	53	53	50	54	50	51	52	55
2	51	52	52	44	54	48	52	52	55
3	51	52	52	42	53	49	50	52	56
4	47	49	49	50	51	38	45	45	48
5	52	53	53	39	54	47	50	51	55
6	51	53	53	32	52	40	45	43	48
7	53	55	54	60	57	53	54	54	58
Mean	51	52	52	45	54	46	50	50	54
Recovery	102%	105%	105%	91%	107%	93%	99%	100%	107%
Std. dev.	1.7	1.9	1.8	8.9	2.1	5.3	3.5	4.0	3.9
RSD (%)	3.4%	3.6%	3.4%	19.6%	3.9%	11.4%	7.1%	8.1%	7.3%
Ottawa sand									
1	52	53	53	62	61	60	55	58	57
2	51	52	53	59	58	53	50	51	52
3	54	54	55	63	61	61	53	57	58
4	52	53	53	62	59	59	52	55	57
5	53	54	54	64	61	58	52	55	55
6	55	55	55	68	61	66	57	60	61
7	53	54	54	62	57	56	51	53	54
Mean	53	54	54	63	60	59	53	56	56
Recovery	106%	107%	108%	126%	120%	118%	106%	111%	113%
Std. dev.	1.2	1.0	1.0	2.7	1.6	4.0	2.5	3.1	2.9
RSD (%)	2.4%	1.8%	1.9%	4.3%	2.6%	6.9%	4.8%	5.6%	5.2%

Table A6. NG and PETN concentrations (µg/kg) found in spiked soils (2 g) extracted with 10 mL acetonitrile for 2 hr and 18 hr in a cooled sonic bath. Target concentration was 50 µg/kg.

	Found concentration (µg/kg)			
	AEC soil		*Ottawa sand*	
Replicate	*2 hr*	*18 hr*	*2 hr*	*18 hr*
NG				
1	54.5	56.6	57.1	64.0
2	43.9	54.5	55.1	58.7
3	48.0	56.6	63.8	66.2
4	38.8	32.1	66.3	61.9
5	52.0	52.4	60.2	64.1
6	51.0	51.3	58.2	71.6
7	43.9	64.1	48.6	61.4
Mean	47.4	52.5	58.5	64.0
Std. dev.	5.5	9.9	5.8	4.1
PETN				
1	61.1	62.8	61.7	65.9
2	48.4	60.8	58.2	59.1
3	53.1	59.9	67.5	68.3
4	42.1	33.9	70.4	62.2
5	58.2	56.7	66.9	62.8
6	57.1	55.9	63.4	74.4
7	47.8	70.1	53.1	61.0
Mean	52.5	57.2	63.0	64.8
Std. dev.	6.8	11.3	6.0	5.2

Table A7. Method detection limits from 25 g Ottawa sand aged 1 hr after spiking and then extracted with 50 mL acetontrile (3,4-DNT internal standard).

	Concentration (µg/kg)							
Replicate	*1,4-DNB*	*1,3-DNB*	*1,2-DNB*	*2,4-DNT*	*4-Am-DNT*	*2-Am-DNT*	*TNT**	*RDX*
1	2.2	2.3	2.1	2.7	2.2	2.7	4.4	7.8
2	1.8	1.6	1.8	2.4	2.0	2.0	5.1	7.2
3	1.5	1.4	1.5	1.7	1.5	1.7	5.4	5.3
4	1.4	1.3	1.5	1.8	1.5	1.7	2.8	5.8
5	1.9	1.8	1.9	2.0	2.0	2.1	10.3	7.1
6	2.4	2.5	2.2	2.4	2.3	2.3	4.3	6.6
7	2.2	2.4	2.1	2.5	2.1	2.2	4.5	7.4
8	2.0	1.7	1.9	2.2	2.0	2.2	12.3	7.5
9	2.0	2.0	1.9	2.2	2.0	1.9	8.6	7.7
10	1.9	2.1	2.0	2.2	2.0	2.0	14.2	8.2
Mean	1.9	1.9	1.9	2.2	2.0	2.1	7.2	7.0
Std. dev.	0.30	0.41	0.23	0.30	0.25	0.30	3.89	0.91
MDL	0.86	1.16	0.64	0.86	0.70	0.84	10.97	2.57
Target conc. (µg/kg)	2.00	2.02	2.06	2.05	2.02	2.01	2.00	8.00

*Ottawa sand extracts contained an interference that co-eluted with TNT.

Table A8. Spike recovery from 25 g Ottawa sand aged 24 hr after spiking and extracted with 50 mL acetontrile (3,4-DNT internal standard).

	Concentration (µg/kg)							
Replicate	*1,4-DNB*	*1,3-DNB*	*1,2-DNB*	*2,4-DNT*	*4-Am-DNT*	*2-Am-DNT*	*TNT*	*RDX*
1	7.6	8.0	8.0	8.7	7.7	8.6	12.7	34.4
2	7.1	7.4	7.4	8.0	6.9	7.7	9.7	30.0
3	8.2	8.5	8.5	9.0	7.7	9.3	13.6	36.6
4	8.2	8.5	8.5	9.2	8.1	9.5	13.2	38.0
5	8.2	8.7	8.7	9.3	7.6	9.6	13.7	42.7
Mean	7.8	8.2	8.2	8.8	7.6	8.9	12.6	36.3
Std. dev.	0.5	0.5	0.5	0.5	0.4	0.8	1.7	4.7
RSD (%)	6.1%	6.4%	6.4%	5.9%	5.7%	9.2%	13%	13%
Target conc. (µg/kg)	10.0	10.1	10.3	10.2	10.1	10.0	10.0	40.0
Recovery	78%	81%	80%	86%	75%	89%	126%	91%

Table A9. Recovery (%) from 25-g soil samples spiked at 10 µg/kg and aged 24 hr prior to extraction with 50 mL acetonitrile.

	Reps	*1,4-DNB*	*1,2-DNB*	*2,4-DNT*	*TNT*	*4-Am-DNT*	*2-Am-DNT*
No soil	1	88%	92%	88%	85%	94%	94%
	2	91%	91%	89%	115%	92%	92%
	1 rep injection	94%	91%	96%	86%	91%	93%
	2 rep injection	97%	94%	106%	123%	90%	90%
AEC	1	35%	45%	39%	54%	43%	interference
	2	16%	20%	*	18%	17%	interference
	3	*	9%	*	*	*	interference
	4	*	18%	14%	16%	13%	interference
	5	*	16%	15%	16%	15%	interference
Silt	1	15%	19%	17%	20%	15%	no peak
	2	15%	17%	17%	17%	15%	no peak
	3	13%	16%	14%	15%	14%	no peak
	4	*	*	*	9%	*	no peak
	5	13%	15%	16%	17%	14%	15%
Wet silt	1	*	37%	*	32%	interference	no peak
	2	*	27%	*	23%	interference	no peak
	3	*	68%	*	69%	interference	no peak
	4	*	84%	*	81%	interference	no peak
	5	*	81%	64%	74%	interference	no peak

*Peak detected, but too small for automatic integration.

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13. ABSTRACT (*Maximum 200 words*)

Nitroaromatic, nitramine, and nitrate ester explosives are analytes of interest for hazardous waste site characterization and land mine detection. Traditionally determined by high-performance liquid chromatography (HPLC), these thermally labile analytes may be determined by gas chromatography (GC) by using direct injection into a deactivated liner and a short (6-m) wide-bore capillary column. Gas chromatography-electron capture detector (GC-ECD) and HPLC-ultraviolet (UV) concentration estimates of these compounds in field-contaminated soils from hazardous waste sites were compared, and excellent correlation ($r > 0.97$) was found between the two methods of analysis for the compounds most frequently detected: 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), 1,3,5-trinitrobenzene (TNB), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). GC-ECD method detection limits (MDL) were about 1 µg/kg for the di- and trinitroaromatics, about 10 µg/kg for the mononitroaromatics, 3 µg/kg for RDX, 25 µg/kg for HMX, and between 10 and 40 µg/kg for the nitrate esters (NG and PETN).

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